

Chemicals and Fuels from Biomass Flash
Pyrolysis - Part of the Bioenergy
Development Program (BDP)

RENEWABLE ENERGY BRANCH

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PREFACE

The present report represents a logical extension of studies reported previously describing the development of the Waterloo Fast Pyrolysis Process (WFPP), and optimization studies carried out in a 3 kg/h small pilot plant unit. The principal objective was to obtain maximum yields of a liquid product that could be used as an alternative fuel oil. Analysis of the liquid product showed that high yields of some unique chemicals were also obtained. In addition, it was found that an easy separation of the crude oil into lignin-derived and carbohydrate-derived fractions was possible. Therefore, further work was carried out to assess this separation method and to attempt to devise methods of recovery for specific chemicals from the crude fractions. In addition, the past pilot plant experience as well as a previously reported economic feasibility study both suggested that scale-up of the WFPP to a process demonstration unit was warranted. The present work described the initial efforts to produce chemicals from the crude pyrolysis oils, and presents a design for a mobile 5 t/day PDU for the WFPP.

In the course of earlier studies as our understanding increased of the nature of fast pyrolysis, new concepts arose. In particular, it was apparent that some feedstocks gave much higher yields of monosaccharides than did others when used in the WFPP. Therefore, experiments were undertaken in an attempt to obtain high monosaccharide yields by appropriate pretreatment of wood or cellulose. Also,

in earlier work, we had been successful in achieving the direct catalytic methanation of wood. The possibility that other hydrocarbons, alcohols etc. might be formed by similar reactions was considered to be worth some preliminary experimentation, and the results of these tests are also reported here.

The studies of recovery of new chemicals from crude pyrolysis oil have not yet led to methods which are economically promising, although technically feasible. On the other hand, two promising new approaches have been developed which rely on variations in the normal WFPP process to produce a different spectrum of pyrolysis products. These new products are readily recoverable in a useable form, and of higher value than the crude oil.

The Waterloo Fast Pyrolysis Process remains as one of the most economically favorable methods of converting biomass to liquid fuel. The crude pyrolysis liquid can also be a source of many chemicals. In addition, three variations of the WFPP now also exist as a result of the work reported here, as well as of previous work. Not only can an alternative fuel oil be prepared, but a process modification allows the production of high methane gas (95% CH_4), another modification will yield solutions of monosaccharides of 150 to 250 g/l concentration, and a third alternative will yield C_2+ hydrocarbons.

As a consequence of these developments, the WFPP represents not only the potentially most economically promising of current thermal conversion processes for biomass, but also the technically most advanced

in concept. The basic WFPP process that produces an alternative fuel oil is now ready for scale-up to demonstration plant size. Therefore, this work should be of interest to both industry concerned with forest or other biomass waste production, and to researchers in this field who are involved in more speculative process development studies.

ABSTRACT

The work described was undertaken to explore the possibilities of recovering specific components or fractions of the pyrolysis oils produced from wood by the Waterloo Fast Pyrolysis Process (WFPP). An extraction procedure using water as a solvent was developed to separate carbohydrate-derived water soluble components from lignin-derived aromatic components. The "pyrolytic lignin" fraction obtained in this way was tested as a replacement for phenol-formaldehyde resin in wood adhesive with encouraging results. The aqueous extract was used as a source of hydroxyacetaldehyde or acetic and formic acids.

It was found that acetic and formic acids could be recovered from the crude pyrolysis oil in good yields by vacuum distillation without thermal degradation of the residue. Calcium acetate/formate could be easily prepared from the distillate, from which acetol could also be recovered. Recovery of hydroxyacetaldehyde from the aqueous extract was difficult, although a number of procedures were attempted. Of these, adsorption in a packed column of hydrophobic molecular sieves appeared to be technically feasible, although further development would be required.

A mild acid pretreatment of wood or commercial cellulose followed by pyrolysis after washing resulted in a pyrolysis liquid high in hydrolyzable sugars and low in acids or other carbonyl compounds. This result represents an alternative to enzymatic hydrolysis for

conversion of cellulose to fermentable sugars, inasmuch as sugar yields (as glucose equivalent) of 75% to 85% of the cellulose can be obtained with solution concentrations of 150 to 300 gm/litre. Further tests will allow an economic assessment to be done, but this process alternative for the WFPP may be of considerable commercial significance.

Preliminary tests were carried out which showed that encouraging yields of C_3 to C_6 olefins could be produced directly by the WFPP. This represents a unique development of this process.

In summary, the Waterloo Fast Pyrolysis Process has demonstrated that a number of selective pyrolytic processes can be carried out by this process. This factor, coupled with great flexibility in accepting a wide range of biomass feed stocks, indicates a wide commercial potential for the WFPP.

EXECUTIVE SUMMARY

Since 1980 a short residence time flash pyrolysis process for the conversion of biomass, peat, coal and other organic materials to liquids has been under development at the University of Waterloo. The process now known as the Waterloo Fast Pyrolysis Process (WFPP), is based on the use of a fluidized bed of sand operating at atmospheric pressure as the pyrolysis reactor. At the optimal temperatures of 480° to 530°C maximum liquid yields of 75% to 80% of the wood fed can be obtained from hardwood or softwood. Organic liquid yields are 60% to 65% of the dry wood fed. These liquid yields are the highest reported for a simple thermal conversion process. The crude liquid pyrolysis oil can be used directly as a fuel in conventional oil burning equipment with only minor retrofitting required. The oil has also been found to contain significant yields of specific components, such as hydroxyacetaldehyde, acetic acid and levoglucosan. The process is very flexible with respect to feedstock, and can produce a liquid product at a low cost and with low capital investment. Details of the process, product characteristics and process economics can be found in previous contract reports.

The present work was undertaken to prepare larger quantities of the crude liquid product and to optimize a fractionation technique to separate the crude oil into an aromatic lignin-derived "pyrolytic lignin" and an aqueous solution containing simple carbonyl and hydroxy compounds derived from carbohydrates. It was hoped to test the pyrolytic lignin as a component of wood adhesives, and to recover

specific compounds, particularly hydroxyacetaldehyde and acetic acid from the aqueous product. Exploratory tests were to be carried out to determine if additional products could be obtained from pretreated wood, and to assist in developing a mechanism for the pyrolytic decomposition reactions. In addition, a few preliminary tests were to be done to explore the possibility of producing C_2+ hydrocarbons by direct catalytic reaction in the fluidized bed, as a follow-up to the successful catalytic hydrogasification process for the production of methane which was developed in our previous work. Finally, a design for a mobile process demonstration unit was carried out by an external engineering consultant, inasmuch as the existing small pilot plant unit (3 kg/h) had been optimized to the extent possible.

The pyrolysis tests were carried out in the laboratories of the Department of Chemical Engineering, University of Waterloo, using the two fluidized bed systems developed in past studies - a bench scale unit with a feed rate of 20 to 100 g/h and a small continuous pilot plant unit with a throughput of 1 to 4 kg/h. Much of the work dealt with further processing of the crude pyrolysis oil, and hybrid poplar wood was used as a standard feedstock in preparing the large quantities required. In addition, various commercial cellulose products were also pyrolyzed. Methods and procedures used in the WFPP have been fully described in earlier reports and in several publications (see General References, Section 10.0).

A simple water extraction technique was found to be adequate for the fractionation of the homogeneous, single-phase pyrolysis oil, which normally contained 15% to 25% water, into a water-rich phase and a water-poor phase. The water-poor phase contained primarily aromatic compounds derived from lignin, and these precipitated and could be readily recovered by filtration or centrifuging. From two to four volumes of water added to the oil was sufficient for a good separation. The lignin product from poplar was recovered and dried to a brown powder, and a sample was tested by Forintek Canada as a component of phenol-formaldehyde wood adhesive formulations. The lignin was used to replace the phenol-formaldehyde resin by either 50% or 70%. Results were encouraging, but the resulting formulation was inferior to phenol-formaldehyde resin alone. However, the lignin should more properly have been used only as a replacement for the phenol monomer in the adhesive, and tests should have been done with an "activated" formulation - that is, one to which formaldehyde or other cross-linking monomer had been added. Therefore, in our opinion, the tests done were far from the optimal use of the lignin, and more appropriate evaluation still remains to be carried out.

An extensive survey of the chemistry of hydroxyacetaldehyde (HA) was made and preliminary test methods for the separation and recovery of HA from either the aqueous fraction or from the crude pyrolysis oil were carried out. Based on the results of these tests, a more detailed investigation of separation by preferential adsorption of hydroxyacetaldehyde on hydrophobic molecular sieves (Silicalite) was

carried out. After initial problems of conditioning the sieves (two different types were used), which contained serious levels of impurities, a series of adsorption equilibrium measurements on the HA-water system were done, followed by column adsorption studies on both synthetic mixtures and pyrolysis solutions. It was found that the equilibrium constant was favourable although not large, in the range of 2 to 3. Acetol, hydroxyacetaldehyde and acetic acid were all preferentially adsorbed on the molecular sieve. Acid conditions had to be maintained to prevent condensation reactions, which normally resulted in about a 7% loss of HA. Elution from the column was done using ethanol or acetone, with the latter being preferable. Tests of adsorbent regeneration by heating at 110° or 750°C, or by steam stripping were carried out and steam stripping appeared to be the best choice, although not completely satisfactory at laboratory conditions. In summary, adsorption on hydrophobic molecular sieves is a technically feasible method of separating hydroxyacetaldehyde from water, but inefficiencies in the process as used in the laboratory would require further process development on a somewhat larger but still bench scale.

Attempts were made to use simple solvent extraction (other than water) to either recover HA, or to separate aromatic and aliphatic fractions. The HA is so readily soluble in such a wide variety of solvents that the search for a uniquely favorable system was not successful. However, as the chemistry of HA is better understood, this method may represent a viable approach. At the present time,

separation of aromatics and aliphatics using water as an extractant appears to be a very effective procedure, and has only the drawback that desirable components such as HA, acetic acid etc. must then be recovered from more dilute aqueous solutions.

Experiments were carried out to determine the feasibility of recovering acetic acid from the pyrolysis products. After various trials, it was established that acetic acid can be recovered by direct vacuum distillation of the crude pyrolytic oil. Simple batch vacuum distillation gave a recovery of 50% to 70% of the acetic and formic acids, and provided the temperature did not exceed 100°C, little degradation of the residual tar appeared to take place. Acetol (1-hydroxy 2-propanone) was also recovered with the acid distillate. Continuous vacuum flash evaporation of the crude oil would reduce the heating period of the residual tar and allow higher recoveries of acetic acid.

When the distillate containing the acetic and formic acids was treated with lime or limestone, calcium acetate or formate was readily formed. Addition of acetone precipitated these two salts in a 95% yield (64% of the original acetic acid). Acetone can be recovered by distillation, and at the same time the acetol can be separated also. If a feasibility analysis is favorable, then acetic acid recovery may be worthwhile on the basis of by-product economics.

Wood and cellulose were pretreated by a mild acid hydrolysis with sulfuric acid at 90°C for various times and at different solid/liquid

ratios. A time of 2 to 6 hours at 90°C with 5% H_2SO_4 and a liquid/-solid weight ratio of 4 appeared to be adequate to solubilize hemicelluloses and to remove ash. When poplar wood hydrolyzed with increasing severity, with the above conditions representing the maximum severity, was pyrolyzed at 500°C in the WFPP bench scale unit, the yield of HA as % of dry feed decreased from 10% to 0.4%, acetic acid from 5.4% to 0.2% while levoglucosan increased from 3% to 30%. For the fully pretreated wood, after separation by water extraction, total sugars as glucose equivalent represented an 84% conversion of cellulose. Similarly, a commercial cellulose (SS-144) also pretreated with acid showed an increase in levoglucosan yield from 7% to 31.8% with a total cellulose conversion to about 81% sugars as glucose equivalent. The same type of result was also found with microcrystalline Avicel cellulose. The resulting aqueous solutions after removal of any pyrolytic lignin could contain from 150 g/l to 300 g/l of sugars if wood was used as a feedstock. In addition, a pentose solution is also obtained from the pretreatment step. If cellulose is used as a feed, a highly concentrated sugar solution can be produced. These results represent a completely new route for the conversion of cellulose and hemicellulose to fermentable sugars which may well be much less expensive than processes based on pretreatment of biomass followed by enzymatic hydrolysis which are now under intensive development. Further work is underway to optimize the pretreatment step for sugar production by pyrolysis, and to investigate the fermentability of the resulting solutions.

Concurrently, a preliminary economic evaluation of this modification of the WFPP will be carried out. At the same time, it is hoped to gain some insight into methods of control of the liquid product spectrum. Results obtained in our laboratory in which the change in liquid product composition with temperature was measured for the pyrolysis of Avicel suggest strongly that levoglucosan or other sugars, or hydroxyacetaldehyde, are formed from cellulose by parallel primary decomposition pathways. It is apparently possible to influence the relative importance of these two pathways by variation of process parameters such as temperature, the presence of catalysts, or by altering the morphology of the cellulose. Although funding is not available for the necessary basic studies to explore the mechanism, some work is going forward in our laboratories.

In earlier work, it was found to be possible to obtain a 75% C-conversion of wood to methane in the WFPP by using a catalytic fluid bed at 550°C and at one atmosphere of hydrogen pressure. The success of this work led to some preliminary tests using other catalysts and process conditions in an attempt to produce other hydrocarbons than methane by direct catalytic pyrolysis. Encouraging results have been obtained using a cellulose feed. Conversions of up to 15% of the feed to C₃, C₄, C₅ and C₆ olefins, dienes etc. have been achieved, which represents about a 30% yield of the maximum theoretically possible. Carbon conversion to hydrocarbons (C₁ to C₆) was about 58%. A number of catalysts have been tested at various operating conditions, and it is anticipated that yields can be improved. These

results represent yet another processing alternative for the WFPP which may yield, after further development, an economical future route for the production of light hydrocarbon liquids from biomass.

A preliminary design of a trailer mounted plant has been completed by BBC Engineering and Research Ltd. The entire process, to handle 200 kg/h of dry biomass, can be mounted on a single low-boy trailer, 12 m long x 2.44 m wide, and includes intermediate storage, shredding, drying, pyrolysis and product collection. The system does not require any site erection and can be operated by two people. The plant includes sufficient automatic control to ensure safe, stable operation. Instruments are provided to measure the data needed for complete mass and energy balances. Additional instrumentation is included to monitor the performance of ancillary equipment for later scale-up. Information will be processed through a data acquisition system. The complete system is estimated to cost about \$926 000, and requires only hook-up of cooling water and electricity.

The proposed PDU is required for several reasons. First, large enough quantities of an alternative fuel oil need to be produced to allow combustion testing in industrial scale equipment. Optimization of the product collection system needs to be completed at a more realistic scale. Long term continuous operating experience of an integrated system is required before commercialization can be expected. If these objectives can be achieved, then a final economic analysis coupled with successful PDU operation will allow final decisions to be made concerning full scale operation.

The current program of work has greatly extended the utility of the Waterloo Fast Pyrolysis Process. It has shown that not only can an alternative fuel oil be produced, but chemicals can be recovered from the crude pyrolysis oil. Two entirely new applications of the WFPP have been demonstrated; the production of sugars from cellulose by pyrolysis, and the direct single-step production of light unsaturated hydrocarbons from cellulose. When these various processing alternatives are coupled with the flexibility of the WFPP in accepting various feedstocks, and with the low capital and operating costs of the process, it is apparent that the potential usefulness of this process for the conversion of biomass to valuable products is much greater than was imagined even a few years ago. At the same time, new and unique areas of research have been opened up by the current program - areas which have the promise of great commercial potential for the future.

CHEMICALS AND FUELS FROM BIOMASS FLASH PYROLYSIS

1. INTRODUCTION TO PRESENT STUDY

Since 1979, a fluidized bed flash pyrolysis process for the production of pyrolytic liquids from biomass has been under development at the University of Waterloo. Initially, a bench scale mini-fluidized bed was developed patterned after that used for the flash pyrolysis of coal. A novel entrained flow low rate biomass feeder was also developed, capable of feeding biomass particles at rates of 5 to 100 grams/hour with an accuracy of 5% (Scott and Piskorz, 1982a). Initial studies done with this bench scale pyrolysis apparatus using maple and hybrid poplar wood showed that up to 65% to 70% yields of organic liquids (75% to 80% total liquid yield) could be obtained from hardwoods at temperatures of about 500°C and 0.5 seconds apparent residence time. Details of this work are given in the final report for ENFOR Project No. C-28 (Scott, 1981), as well as in several publications e.g. Scott and Piskorz (1982b), Scott et al. (1985). In the course of bench scale work, the effects on the liquid yield of particle size, residence time, reaction atmosphere and of various additives were reported. In addition to maple and poplar wood, wheat straw, corn stover, poplar bark, bagasse and peat moss were also evaluated for conditions giving maximum yields of liquids (Scott et al., 1985).

As a result of the promising results obtained in the bench scale work, funding was received in April, 1981, to design, construct and

operate a larger continuous unit with a throughput of 1 to 3 kg/h of biomass (ENFOR Project C-223). This work was completed in early 1983, and has been reported (Scott, 1983, 1984a; Scott and Piskorz, 1984a).

Additional work was undertaken in 1983 to 1984 to extend the knowledge of the nature of the pyrolysis products, how these products might be altered to a more desirable liquid fuel, and to participate in the International Energy Agency Biomass Direct Liquefaction Test Facility Evaluation Program (IEA BLTF project). Extensive work was done on chemical modification of the liquid product, both by liquid phase and vapour phase reactions. Additional pilot plant tests were done in the IEA program both to give a better picture of possible yields, and to supply the required quantities of pyrolytic oil for other tests. Pilot plant runs were done using whole tree poplar aspen wood in order to obtain pyrolytic oil samples which might be more representative of those produced in a larger scale unit. All this work has been described in a major contract report (Scott, 1984b) and in publications (Scott et al., 1985; Scott and Piskorz, 1984b).

The work on the Waterloo Fast Pyrolysis Process was resumed in January, 1984, when additional funds were received from the National Research Council (later transferred to the Renewable Energy Division of Energy, Mines and Resources). In late 1984, funds were received from the Strategic Grant Program of the Natural Sciences and Engineering Research Council for the purchase of a GC/MS unit as well

as an HPLC unit (jointly with Prof. M. Moo-Young). This equipment became operational in April, 1985, and has played a major role in the characterization studies of the oils produced from the Waterloo Fast Pyrolysis Process.

A major final contract report (Scott, 1986) described a considerable degree of progress in the understanding of and technical evaluation of the process now known as the Waterloo Fast Pyrolysis Process (WFPP).

An extensive series of pilot plant tests, using a whole tree poplar feed, was carried out according to an optimal statistical plan. The variables studied were temperature, residence time and feed rate. The latter two could be varied only over limited ranges because of both equipment design limitations and the limitations of good fluidization behaviour. The tests for statistical significance showed clearly that in terms of yield of organic liquid, the temperature of reaction was the single most important variable. Within the feasible operating ranges, neither feed rate nor residence time were as important. Optimal conditions were determined to be, for poplar wood at least, 500° to 525°C, 0.4 to 0.6 seconds residence time and a feed rate up to about 3.0 kg of dry wood per litre of expanded bed volume.

A kinetic model of the reactor was developed based on a simple scheme of two parallel decomposition reactions to volatiles or to char + gas; with a second consecutive decomposition step of the volatiles to

gases (very little secondary char is formed in the WFPP). With an assumption of first order kinetics, this model successfully described the yield of liquid product from about 450° to 850°C (Lidén, 1985; Scott et al., 1987).

A detailed study of lateral mixing in shallow fluidized beds was carried out, and a new mixing coefficient correlation proposed. A mixing model was also proposed which appeared best to fit the observed phenomena. The techniques developed in these studies were then used to measure the mixing behaviour of mixtures of low and high density solids in fluidized beds, and to measure the residence time distribution of wood particles in a fluidized bed of sand. These latter values were then employed in testing the kinetic model (Berruti, 1985; Berruti et al., 1986; Lidén et al., 1987).

In brief, the WFPP operates at optimal conditions so that biomass feed particles and sand particles are always fully mixed in the fluid bed, and the wood particles are never eluted from the bed. However, as pyrolysis proceeds the wood particle loses 80% to 90% of its mass, but retains much of its original geometric shape. When the density of the particle is low enough, it is eluted from the bed, a process representing particle mean residence times of 2 to 6 seconds. The system is therefore self-regulating, in that biomass particles are retained in the bed until they are fully reacted. Volatiles liberated are swept from the bed with a mean vapour residence time of about 0.6 seconds.

Other aspects of the WFPF process investigated included the effect of moisture content of the feed. Except as a diluent and possible heat sink, there is no chemical effect of moisture content at optimal conditions up to at least 25% moisture. Spruce sawdust and mill waste were pyrolyzed with organic liquid yields very similar to those obtained from hardwoods. Some differences in liquid product acid content were noted for the two cases, however (less acetic acid and more formic acid were obtained from softwood).

Preliminary tests on the genotoxicity of pyrolysis oils were carried out by the Environmental Monitoring Division of the British Columbia Cancer Institute of Vancouver, B.C. Tests for carcinogenic properties showed very little effect, with only a narrow dosage range showing an effect of marginal statistical significance. Preliminary tests of mutagenicity again showed some effects in a narrow dosage range. In summary, more extensive testing would be required for a clear assessment, but preliminary results show surprisingly low genotoxicity of this oil. These results are in agreement with similar tests done by U.S. workers.

Electrostatic precipitation was tested as a means of collecting the oil fog normally formed when pyrolysis volatiles are quickly cooled. Because of the highly polar nature of the pyrolysis product, it can be very easily collected with a very high efficiency at low (non-corona) voltages in a simple collector. Electrostatic precipitation is now used routinely in the bench scale apparatus.

A great deal of work was carried out characterizing pyrolysis oils after the acquisition of HPLC and GC-MS analytical equipment. As a result of these studies, about 90% of the liquid product has been quantitatively identified. About 20% to 25% is water, 18% to 25% is derived from lignin, and the balance is derived from cellulose primarily, and to a lesser extent from hemicellulose. Of the individual compounds identified, the presence of anhydrocellobiosan as the major disaccharide product was demonstrated for the first time (Radlein et al., 1987a). Significant amounts of hydroxyacetaldehyde (up to 15% of the oil) were also present, and suggest this compound as a major potential commercial chemical. The presence of such large yields also led to the publication of some speculations concerning the mechanisms of fast pyrolysis of cellulose (Piskorz et al., 1986).

The lignin fraction of the pyrolysis oil can be readily separated and recovered from the carbohydrate fraction by water extraction. This lignin product gave an NMR spectra which was essentially identical to that obtained from the lignin recovered from steam exploded poplar wood (Radlein et al., 1987b). The aqueous carbohydrate fraction has a sugar content such that it may be a very economical substrate for a fermentation process.

A conceptual preliminary and economic feasibility study was carried out by BBC Engineering Ltd. (Toronto). This study was based on a 100 dry t/day or 500 dry t/day plant size, and assumed a feed of green wood waste at 40% moisture at a cost of \$40 per dry tonne. Scale up

rules might be adequate for a 100 t/day fluidized bed reactor, but at 500 t/day feed rate, probably a circulating fluid bed might be a better choice. This option is now being investigated experimentally on a laboratory scale. Approximately one third of the capital cost goes for wood grinding, about one third for wood drying and handling, and about one third for the actual pyrolysis unit. The cost of the wood feed is a major operating cost - about 50% for a 500 t/day plant and about 30% for a 100 t/day unit.

On the basis of a 50% equity and a 30% DCF rate of return, the cost of production of a pyrolysis oil (about 24% water) would be about \$92/tonne or 10.8 ¢/litre (S.G. = 1.18) or \$5.7/million BTU. This production cost would be \$8 to \$9/million BTU for a 100 tonne/day plant, if the same conceptual design and economic criteria were used (Scott, 1986).

In another report of research, it was shown that if the sand in the WFPP fluidized bed reactor is replaced with an appropriate catalyst, and a hydrogen atmosphere is used, that wood can have a 75% carbon conversion to methane to produce a gas containing 95% methane. This development led to a proposed new conceptual gasification process for wood which requires no inputs other than wood and energy to produce a synthesis gas (Garg et al., 1987).

In summary, previous work has shown that the WFPP is an efficient, low cost process for producing an alternative fuel oil. In addition, the crude pyrolysis oil contains several valuable chemicals in

significant amounts. Further, the product spectrum can be altered by changes in process conditions, by the use of catalysts, or by the pretreatment of feedstock. All of these modifications can be carried out in the same process unit with minor differences. The WFPP, therefore, is not one process but a group of processes, which can produce a wide variety of products. However, some of these processes are still in the research or laboratory development stage, and most of the work reported here describes further progress in these new versions of the Waterloo Fast Pyrolysis Process.

2. OBJECTIVES

Inasmuch as the program of research which is reported here is to some degree a continuation of earlier studies, this fact is reflected in the objectives. Two new concepts were investigated for the first time in this work, however, both with encouraging results. Principal objectives were:

1. Preparation of larger quantities of crude pyrolysis liquid in the Waterloo Fast Pyrolysis Process pilot plant from poplar and from spruce, and the fractionation of these liquids by an extraction procedure into carbohydrate-derived or lignin-derived fractions;
2. Testing of lignin fractions as a component of wood adhesives;
3. Development of separation procedures to recover chemicals from the carbohydrate-derived fraction, and in particular, hydroxyacetaldehyde and acetic acid, together with other compounds if feasible;
4. Pyrolysis of pretreated wood (mild acid hydrolysis) or a commercial cellulose to determine changes occurring in liquid product composition, and to assess possible uses of the liquid product. Tests to be mainly exploratory in nature;
5. Investigation of in situ catalytic methods in the WFPF to see if C_2 to C_6 hydrocarbons could be produced directly from wood or cellulose. Tests to be only exploratory in nature;

6. To sub-contract for a design for a 5 dry t/day mobile fast pyrolysis unit which would serve as a Process Demonstration Unit (PDU).

The original statement of objectives allowed for either the final objective above (PDU design) or the collection of additional pilot plant data. In view of the large amount of pilot plant data already available, it was decided after consultation with the scientific authority, to elect the PDU design option.

All of the above objectives have been completed more or less as proposed. The success of two of these objectives (4 and 5) are likely to lead to the development of new process modifications for the WFPP.

3. METHODS AND PROCEDURES

The apparatus employed in the current studies has been described in earlier publications, and details can be found there. Both the bench scale (30 to 100 g/h) fluidized bed unit and the 3 kg/h pilot unit were used for the various tests. Descriptions and procedures used as well as analytical methods can be found in journal articles by Scott and Piskorz (1982)(1984)(1985) or in previous final contract reports (Scott, 1983, 1984, 1986).

Because a variety of methods were employed in various aspects of this work, any unique apparatus and procedures used will be described in the "Results" section dealing with the particular subject.

4. RESULTS AND DISCUSSION

4.1 Introduction to Recovery of Chemical Components

The yields of products from the pyrolysis of four woods, carried out in earlier work, are shown in Tables 4.1 and 4.2 in order to show the nature of the chemicals contained in the crude pyrolysis oil. The values given are as percentages of the dry wood weight fed. Some compounds are present in significant amounts, for example, hydroxyacetaldehyde yield varies from 8.8% to 12.9% of the crude oil product, while acetic acid yield is of the order of 7.0% to 9.0%, with formic acid content at a similar level. Glyoxal, which can be readily distilled off, is present at about 2% to 3% in the oil.

The phase diagram shown in Figure 4.1 is the basis for the primary fractionation method used. The original conceptual fractionation scheme is shown below, with the first stage being a water extract. This primary separation was tested extensively, and is now used as a routine analytical and preparative procedure in our laboratory. An illustration of the primary extraction method for a crude pyrolysis oil from eastern white spruce is shown in Figure 4.2.

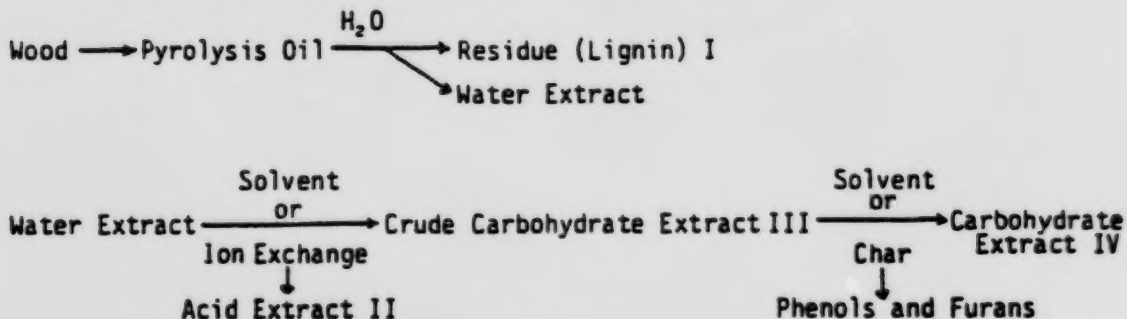


Table 4.1

Pyrolysis Yields from Different Woods

	Brockville Poplar			White Spruce			Red Maple			IEA Poplar		
Run #	51	58	50	42	43	44	14	63	81	27	59	A-2*
Temperature, °C	497	504	555	485	500	520	532	508	515	500	504	497
Moisture content, wt%	+	5.2	+	+	7.0	+	3.8	5.9	9.5	6.2	4.6	3.3
Particle Top Size, µm	+	1000	+	+	1000	+	590	590	1000	590	1000	590
Apparent Residence Time, sec	0.64	0.47	0.57	0.70	0.65	0.62	0.69	0.47	0.44	0.55	0.48	0.46
Feed Rate, kg/hr	2.24	2.10	4.12	2.07	1.91	1.58	2.16	1.98	1.32	2.24	1.85	0.05
Yields, wt% of m.f. wood												
Organic liquid	62.9	62.9	59.0	63.1	66.5	66.1	67.3	67.9	65.0	65.8	66.2	65.7
Water	10.3	9.7	10.2	10.7	11.6	11.1	7.4	9.8	10.0	9.3	10.7	12.2
Char	14.4	16.5	10.6	16.3	12.2	12.3	9.0	13.7	12.1	12.1	11.8	7.7
Gas:												
H ₂	0.02	0.02	0.07	0.04	0.02	0.01	0.04	0.01	0.02	0.02	0.01	--
CO	4.95	4.71	8.40	4.16	3.82	4.01	6.96	4.12	4.83	5.32	4.44	5.34
CO ₂	6.14	5.89	7.06	3.38	3.37	2.69	4.02	4.89	5.36	6.30	5.75	4.78
CH ₄	0.45	0.44	0.97	0.34	0.38	0.43	0.75	0.36	0.57	0.48	0.37	0.41
C ₂ H ₆	0.22	0.19	0.40	0.16	0.17	0.16	0.24	0.16	0.21	0.20	0.13	0.19
C ₂ H ₄	0.06	0.05	0.11	0.02	0.03	0.05		0.04	0.07	0.04	0.05	--
C ₁	0.06	0.07	0.10					0.07	0.10		0.08	0.09
C _n	0.13	0.16	0.28	0.03	0.04	0.06	0.04	0.14	0.41	0.09	0.19	3.10
Total Gas	12.0	11.5	17.4	8.1	7.8	7.4	12.1	9.8	11.6	12.4	11.0	10.8
Overall recovery wt%, m.f.	99.7	100.5	97.2	97.8	97.7	96.7	95.7	101.2	98.7	99.7	99.8	96.4

* Bench Scale Unit

Table 4.2

Analysis of Liquid Products

Run #	Brockville Poplar	White Spruce	Red Maple	IEA Poplar
Temperature	504	500	63 508	A-2 504
Yields, wt% of feed, m.f.				
Organic liquid	62.9	66.3	67.9	66.2
1. oligosaccharides				0.70
2. cellobiosan	1.11	2.49	1.62	1.30
3. glucose	0.55	0.99	0.64	0.41
4. fructose	1.34	2.27	1.51	1.32
5. glyoxal	1.42	2.47	1.75	2.18
6. methylglyoxal				0.65
7. levoglucosan	2.52	3.96	2.84	3.04
8. 1,6 anhydroglucofuranose	--	--	--	2.43
9. hydroxyacetaldehyde	6.47	7.67	7.55	10.03
10. formic acid	5.40	7.15	6.35	3.09
11. formaldehyde	--	--	--	1.16
12. acetic acid	6.30	3.86	5.81	5.43
13. ethylene glycol	0.87	0.89	0.63	1.05
14. acetol	1.70	1.24	1.15	1.40
15. acetaldehyde	--	--	--	0.92
16. methanol	--	--	--	--
Water-solubles-total above	27.7	33.0	29.9	34.2
Pyrolytic lignin	24.8	20.6	20.9	16.2
Amount not accounted for (losses, water soluble phenols, furans etc.)	10.5	12.9	17.1	15.8

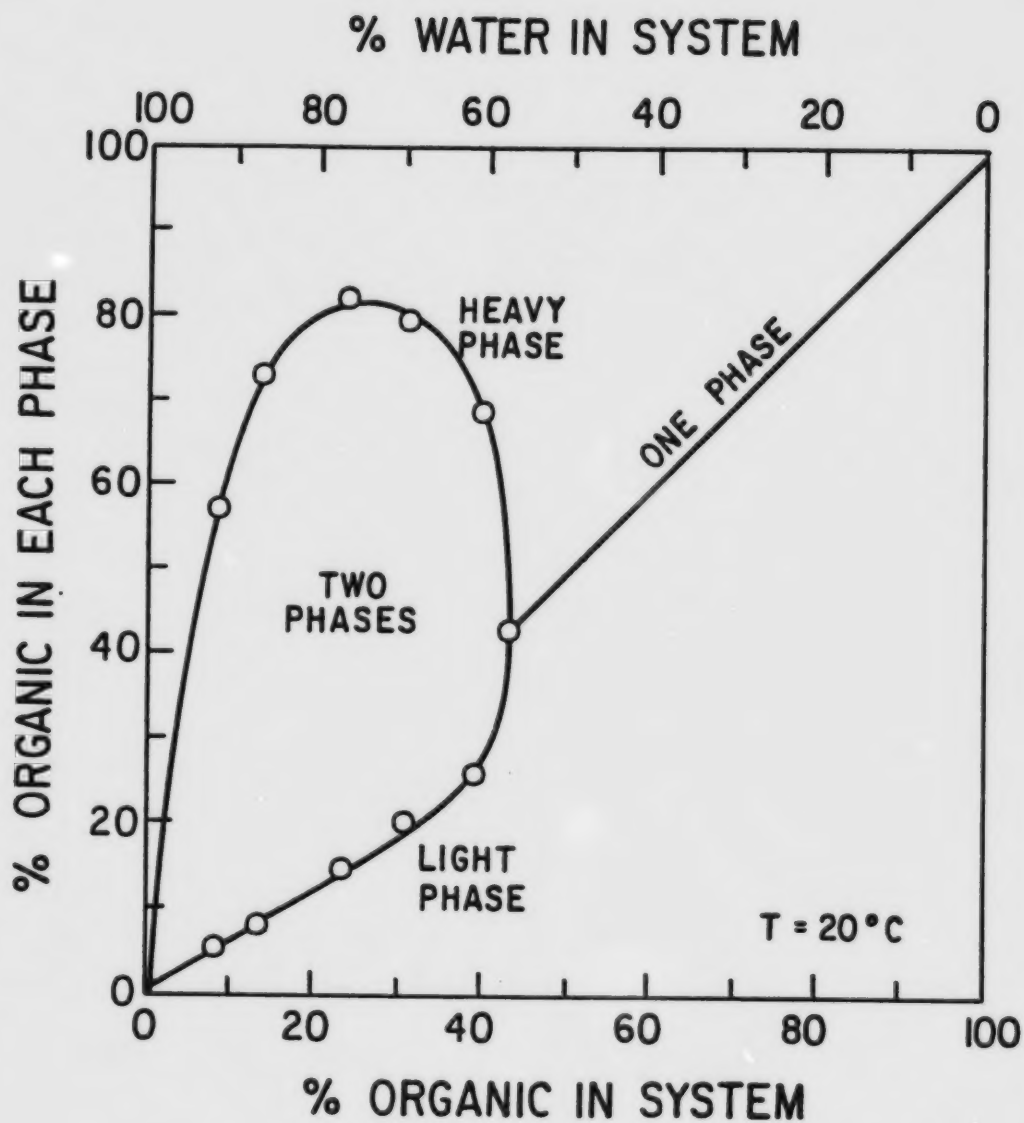
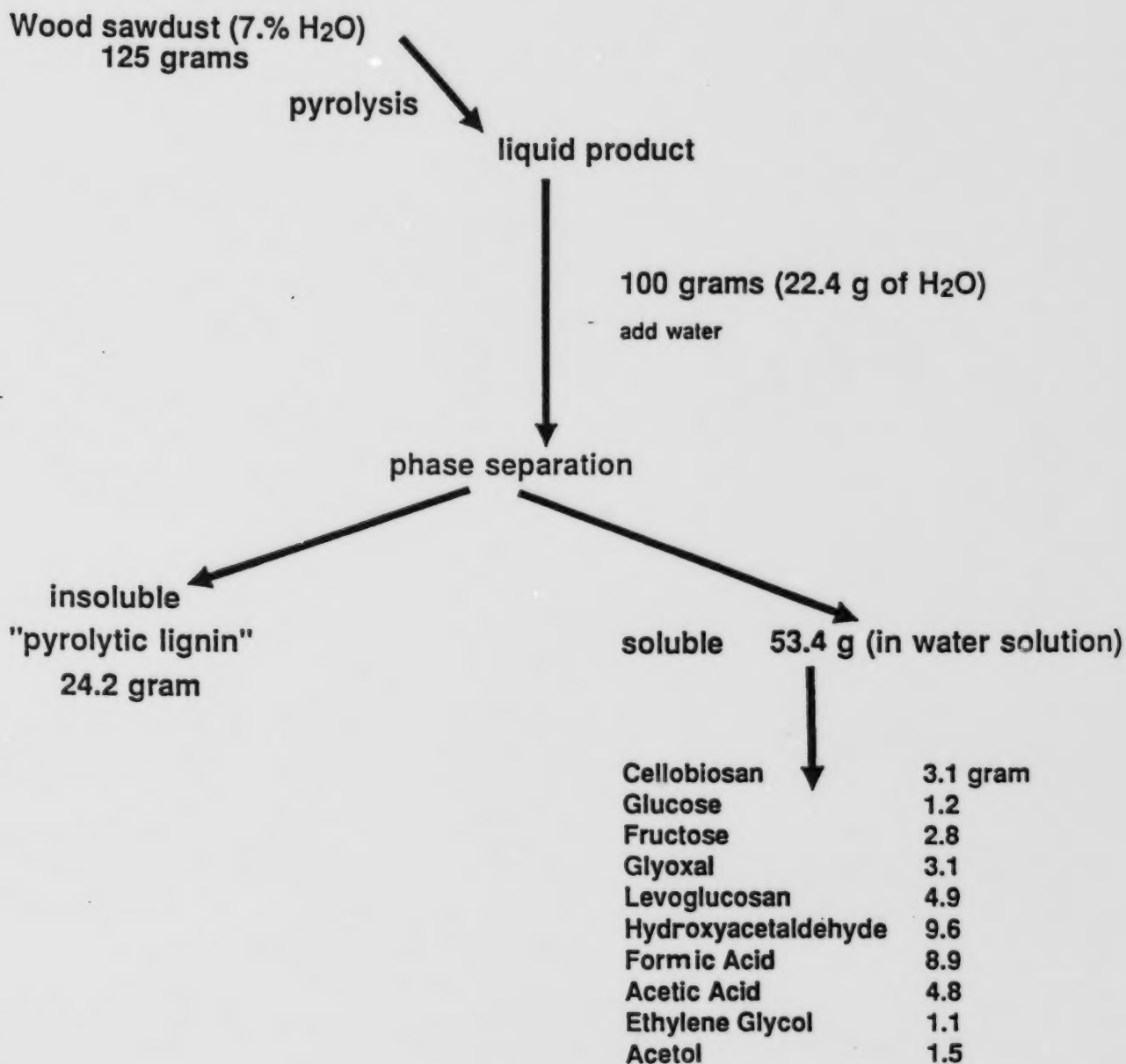


Figure 4.1

Phase Diagram for Wood Pyrolysis Oil from Poplar with Water at 25°C

Separation of Liquid Product from Eastern Spruce 15



Final balance of Liquid Product

"lignin"	24.2	
water	22.4	
organics soluble in water	53.4	41.1 gm clearly identifiable
	<u>100.0</u>	gram

The ratio of water added was usually 2 volumes of water to one volume of crude tar. On the basis of 20% water in the crude tar, this represents an extraction ratio of about 2.3 water/tar by weight to yield a final solution containing 70% water overall. Reference to Figure 4.1 will show that a two phase mixture results, with one phase containing about 82% organics and the other about 16% organics. The water-poor phase is an insoluble precipitate that can be readily filtered, dried and crushed to a fine brown powder. NMR spectra show that this material is a degraded lignin product, very similar to steam exploded lignin in functionality. The aqueous extract contains most of the water soluble compounds as well as some compounds of limited solubility in water such as phenols or furfurals. By varying the amount of water extractant used, the amounts of these latter compounds in the aqueous phase could be varied.

Tests were carried out on a small scale to accomplish a further fractionation of the water extract. If ion exchange was used to remove acids followed by a charcoal adsorption step (to remove phenols and higher molecular weight compounds), a final extract solution (Extract IV) was obtained which was water-white to pale yellow in colour. This extract contained sugars, ketones, aldehydes and other carbonyl compounds derived from the holocellulose fraction of the wood. This general extraction procedure, in whole or in part, was used in preparing fractions for analysis or for further component

recovery tests. (For analysis, the charcoal adsorption step was not used, because some lower molecular weight water soluble compounds were also removed.)

The recovery of hydroxyacetaldehyde from these extracts or from the crude oil presents some severe problems. This compound is very reactive, and if heated, especially in basic solution, it rapidly undergoes condensation reactions. In solution it normally exists as a dimer. It is very polar in nature and highly soluble in water.

As a consequence, the first attempts at recovery of hydroxyacetaldehyde were based on the need to separate it from the water solution and then to isolate it from a suitable solvent. The recent commercial availability of hydrophobic, controlled pore size, solid adsorbents such as Silicalite suggested that an adsorption step might be entirely feasible. Accordingly, a fairly detailed study of the nature of this adsorption process was undertaken. It was also apparent that if a direct extraction of the hydroxyacetaldehyde into a non-aqueous solvent could be successfully carried out, then this would also be a possible separation method. A third alternative was the extraction or precipitation of the lignin fraction by the use of a solvent, thus leaving a much more concentrated solution of hydroxyacetaldehyde in the residue since no additional water would be added. The next section is a report by Dr. D. Radlein

on the preliminary work carried out to test these various possibilities, and to generally review the chemistry of hydroxyacetaldehyde. Following this discussion is a report by Dr. S. Czernik on the extensive laboratory testing done to evaluate further the most promising methods, in particular, separation by selective adsorption.

4.2 A Review of the Chemistry of Hydroxyacetaldehyde (HA)
and Its Isolation from Pyrolytic Tars

by D. Radlein

Dept. of Chemical Engineering, University of Waterloo

Various ideas for methods of separation and isolation of HA from pyrolytic tars were explored. It was assumed that if HA was obtained from pyrolysis of wood the first stage of treatment of the tar would be precipitation of lignin by dilution with water. Preliminary experiments showed that the ratio of water to tar for efficient precipitation of lignin is from about 2:1 to 4:1 so that HA concentrations in the aqueous solution would be 2% to 5%. (Alternatively, if it was economical to produce HA by pyrolysis of cellulose, it would be available in concentrations perhaps as high as 20%.) The experiments described below were all for the purpose of making preliminary assessments and so are, for the most part, non-quantitative.

Potential methods investigated were:

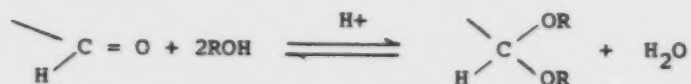
- A. Reversible conversion to a volatile distillable derivative;
- B. Reversible conversion to a crystalline derivative for separation by fractional crystallization;
- C. Steam distillation;
- D. Adsorption;
- E. Chromatographic separation;
- F. Membrane separation;
- G. Irreversible chemical conversion to other substances;
- H. Metal chelation.

In addition, the possibility of effectively irreversible conversion to some other useful and perhaps more easily separated compound was considered, although not investigated experimentally. These will be discussed after presentation of the experimental observations.

A. Volatile Derivatives

Such derivatives must satisfy a number of criteria: (i) they should form readily; (ii) the derivatising agent should be relatively stable, cheap and perfectly recoverable; (iii) the derivative should be sufficiently volatile for separation by conventional distillation; (iv) the reaction should be easily reversible.

Examination of the literature showed that the only compounds which meet most of these criteria reasonably well are the acetals, with the dimethyl acetal being the most volatile. Acetals form readily from aldehydes and alcohols in the presence of strong acid catalysts and the reaction mixture exists as an equilibrium mixture.



In an early work [1] the equilibrium constant for the formation of the dimethyl acetal of HA was found to be $K = 0.0202$. Thus its formation would be enhanced only if the water content was reduced to fairly low levels. The boiling point of the dimethyl acetal is 158° to $159^\circ\text{C}/749$ mm Hg [2].

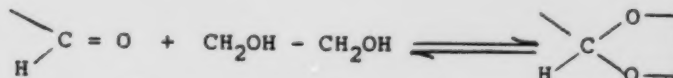
Many different catalysts have been shown to be effective for acetalization and include: (i) alcoholic HCl; (ii) ZnCl_2 ; (iii) anhydrous CuSO_4 ; (iv) p-toluene sulfonic acid; (v) acid zeolites; (vi) protonated forms of cation exchange resins.

Water is usually removed by azeotropic distillation with benzene. (The azeotrope boils at 69°C and contains 91% benzene and 9% water while at 20°C it separates into an organic and an aqueous phase. The former contains 0.06% water and the latter 0.07% benzene.)

In one interesting report [3] various acetals were synthesized by dissolving the aldehyde in the relevant alcohol and heating in the presence of hydrophilic (and acidic) molecular sieves, e.g. mordenite and zeolite A. The zeolite functioned both as a catalyst and as an adsorbent to remove water formed. This suggests the following intriguing possibility in our case. Use of a hydrophobic small pore molecular sieve (Silicalite) with a homogeneous acid catalyst would presumably selectively exclude water and lead to formation of acetal which would be strongly

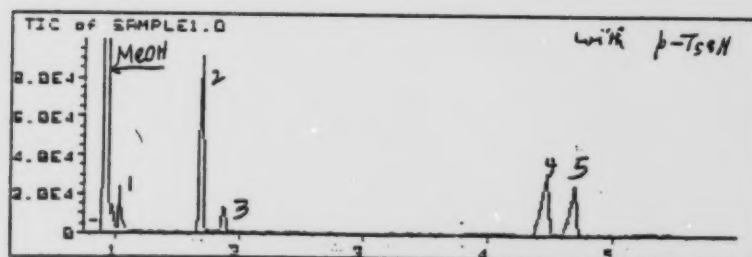
retained within the pores. The acetal could then be directly fractionally distilled from the solid after removing the liquid.

Finally mention should be made of the cyclic acetals (1,3-dioxolanes) which form from 1,2-diols like ethylene glycol [e.g. see 4]. These form much more readily than regular acetals and in most cases do not even require catalysis. Since ethylene glycol boils at 198°C it would be possible to selectively distill off the water followed by the dioxolane of HA from the solvent



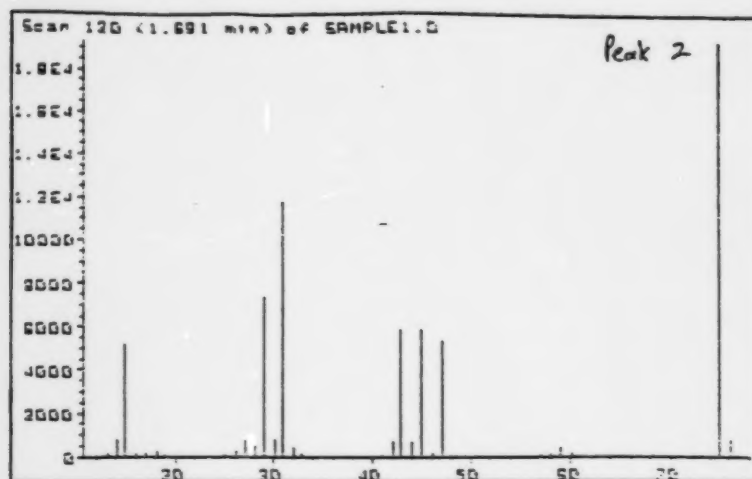
(N.B. Peak 6 in the GC-MS chromatogram in the addenda to the lignin paper is probably the 1,3-dioxolane of ethylene glycol and HA.)

The ease of formation of the acetal of HA was investigated experimentally. Pure HA was dissolved in methanol and a small quantity of p-toluene sulfonic acid added as catalyst. The solution which was maintained at room temperature was analysed within 10 mins. by GC-MS. The result was:



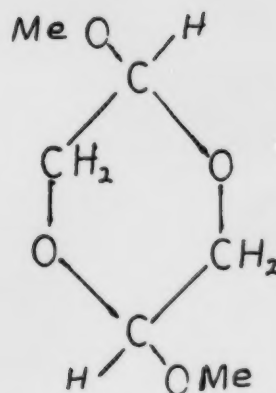
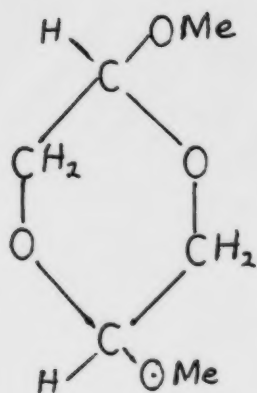
(He at 55 cm/min., 10°C for 5 mins., then 10°C/min.)

Peak 1 is unchanged HA. Peak 2 has the MS shown below.

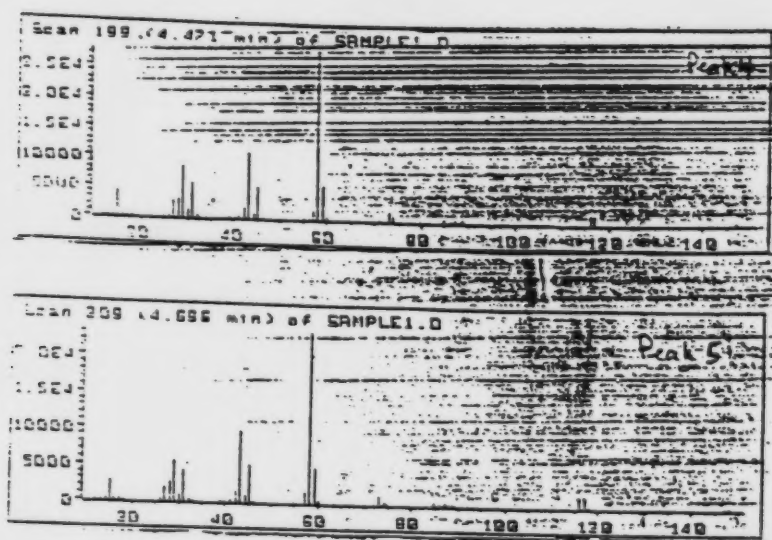


Although the molecular ion at $M = 106$ was not detected, the strong peak at $M = 75$ indicates this is in fact the acetal. (Acetals are known to fragment readily by loss of OR; in this case $OR = OMe$, $106 - 31 = 75$.)

Peaks 4 and 5 show essentially identical MS and are therefore probably (optical) isomers. This observation and the presence of the apparent molecular ion at mass 148 suggest strongly that they are the cyclic acetals.



(MW = 148)



These would form by condensation of two hemi-acetals of HA.

It was further observed that Peaks 4 and 5 grew with time at the expense of Peak 2.

To examine the possibility of forming a distillable acetal from the aqueous extract of the tar a sample of "liquid smoke" was investigated. This was an aqueous extract which remained open on the bench for several months to allow evaporation of water.

It was dark brown and proved impossible to clarify with charcoal but it showed a similar LC pattern to a fresh sample. It was dewatered to 4.55% H_2O by vacuum evaporation at 60°C. 0.5 g of p-toluene sulfonic acid and 4.8 g of liquid smoke were dissolved in excess of methanol. The mixture was then heated and methanol distilled off continuously with simultaneous addition of fresh dry methanol. In this way water was gradually removed. The concentration of water in the initial methanol distillate was 21.1 mg/g. When this had fallen to near the level in the methanol added (4.2 mg/g) all the methanol was distilled off.

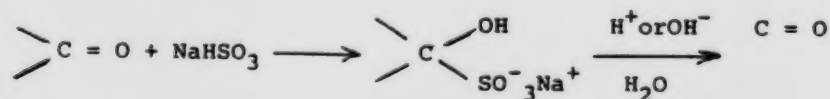
The remaining material was an extremely gummy dark brown mass that had apparently undergone extensive polymerisation. This was perhaps to be expected in view of the presence of so many hydroxylated carbonyl compounds in the mixture. In view of this no attempt was made to distill the material (although, in retrospect, this ought nevertheless to have been tried).

It was concluded that it is unlikely that HA can be separated by acetalization in the usual way. However the method based on hydrophobic molecular sieves and discussed above seems worth investigating. It would offer two principal advantages: (a) it would be possible to carry out the reaction directly in dilute aqueous solution; and, (b) polymerization would be inhibited by size restrictions in the zeolite pores.

B. Crystalline Derivatives

(i) Bisulfite

The most promising candidate here would be bisulfite compounds. These form readily in aqueous solution from carbonyls and sodium bisulfite



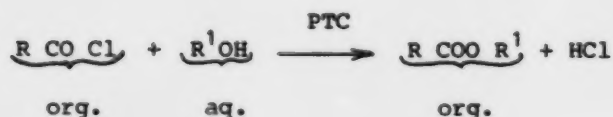
As indicated, the carbonyl compound can be recovered by hydrolysis with strong acid or base. In some cases the bisulfite compound will precipitate from aqueous solution. However it has been reported that the bisulfite of HA is very water-soluble [5]. This was verified experimentally. Thus this method could only be applied by first distilling off water or perhaps the bulk of it, dissolving in a suitable solvent (e.g. acetone or methanol) then progressively precipitating the bisulfites by addition of a suitable proportion of a hydrophobic organic solvent e.g. toluene. It should be realised however that all carbonyl compounds form bisulfites and so efficient fractionation may not be possible. One might also envisage micellar extraction of the bisulfite directly from the aqueous solution into an organic phase using a suitable surfactant. Selectivity problems might however be even worse. None of these aspects were investigated any further.

A disadvantage of the use of a bisulfite is that, even if successful, one would end up with an aqueous solution containing inorganic ions and the separation of HA from such a solution would still have to be faced.

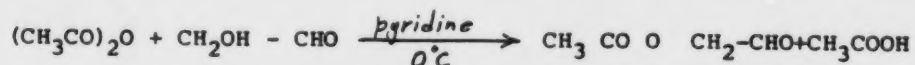
(ii) Esters

Another approach entailing the reversible formation of a crystalline derivative is the formation of an ester. This is one of the few reactions which can exploit the hydroxyl instead of the reactive carbonyl group. However ester formation requires anhydrous conditions. A novel approach to deal with this problem could be that described in Refs. 6 and 7, in which an acid chloride is dissolved in an organic phase (e.g. toluene or chlorobenzene) together with a suitable phase transfer catalyst - Aliquat 336 (tricaprylmethylammonium chloride) appears to be suitable as it is inexpensive and virtually insoluble in water. When contacted with a dilute aqueous solution of phenols the corresponding esters were readily formed and extracted into the organic phase.

There seems no reason why such an approach should not work for HA.



Thus acetyl chloride is cheap (US\$23.20/kg from Sigma) and comparable in price to acetic acid. The acetate has also been prepared [8] directly from HA and acetic anhydride which is an alternative (and cheaper ~ \$13/kg) acetylating agent.



The acetate has a good high melting point of 158°C suggesting good crystallisability.

To apply this method it may be necessary to remove acids first. While other hydroxylated compounds may also react it is expected that HA should be much more efficiently extracted than, say, sugars since it has only one hydroxyl group. It should be possible to effect further purification by fractional crystallisation.

Note, however, that hydrolysis of the ester back to HA will generate acetic acid by-product which would involve further separation. An alternative ester is the benzoate from benzoyl chloride which is much more expensive (\$137/kg) but would perhaps give a more readily crystallized ester.

C. Steam Distillation

HA is known to be relatively volatile for a sugar [5]; thus it can be distilled under vacuum as low as 90°C. Its steam distillation was therefore attempted.

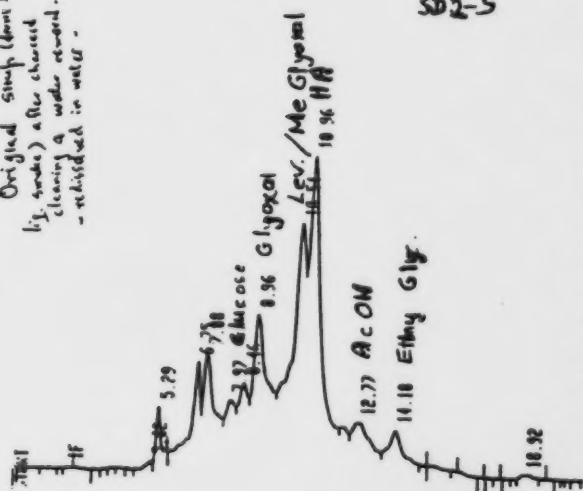
Initially saturated steam from the steam line was used. This showed extremely poor efficiency although some distillation was observed. Accordingly an improved apparatus was constructed in which the steam from the laboratory steam line was heated in a furnace to give a dry superheated steam at about 350°C. This steam was then passed into an insulated flask containing a sample of pyrolysis oil and the vapour generated was condensed in a standard laboratory water-cooled glass condenser.

A sample of 20 g of "liquid smoke" (LS) which contained 14.7% H₂O was dissolved in 20 g H₂O. The LS had the HPLC trace shown below (sample SD2-S) and the analysis on the following page.

Resolution was poor.

Original sample (from 2.0
l.g. smoke) after charcoal
cleaning & water removed.
- redissolved in water -

SD2-S



RUN # 718
WORKFILE ID: C1
WORKFILE NAME:
ID: 0
NO ISTD PK MATCH

AUG/03/86 16:05:00

AREA	RT	AREA	TYPE	AR/HT	AREA
5.62	4912	PP	0.081	0.041	
5.29	183160	PB	0.174	1.571	
6.75	572660	BV	0.389	4.781	
7.08	969000	VV	0.468	8.090	
7.97	469350	VV	0.419	3.919	
8.46	631520	VV	0.426	5.273	
8.96	1799200	VV	0.622	15.021	
10.54	2795900	VV	0.582	23.343	
10.96	3433800	VV	0.555	28.668	
12.77	652400	VV	0.883	5.448	
14.18	411460	VV	0.604	3.435	
18.92	49229	VV	0.477	0.411	

HPLC Analysis of Liquid Smoke Derivatives

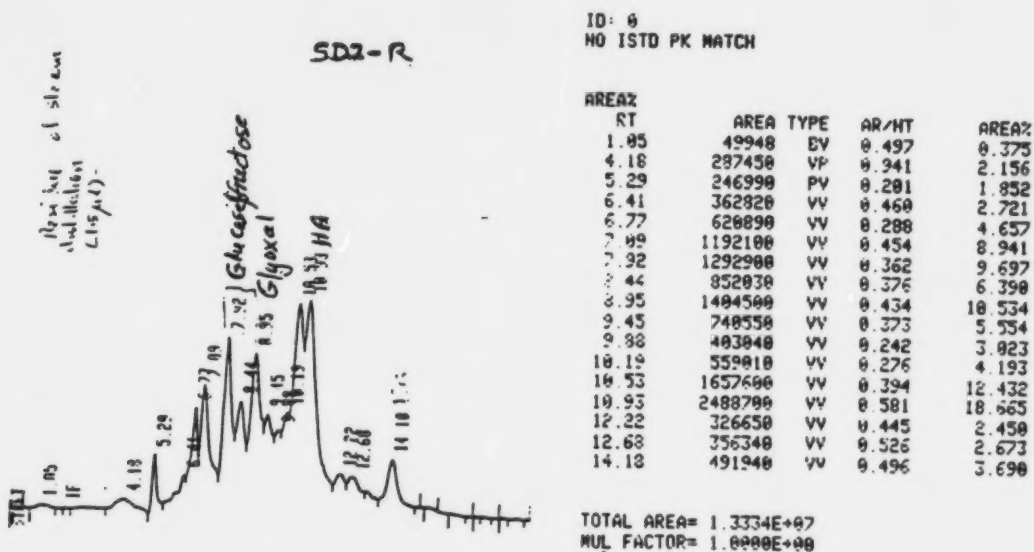
Compound Name	Sample Description			
	SD2-R	SD2-S	SD2-D*	SD2-D*
Glucose	2.0	2.6		
Fructose	1.4	3.3		
Glyoxal	1.9	7.7		
Levogluconan**	2.7**	14.6**	45.5	58.8
Hydroxyacetaldehyde	4.4	18.0		
Acetic Acid	1.5	7.9	12.8	10.3
Ethylene Glycol	1.5	6.4		1.8
Acetol				
Unknowns				
Total				
Moisture (K.P.)	71.9%	14.67%		

* Very poor resolution.

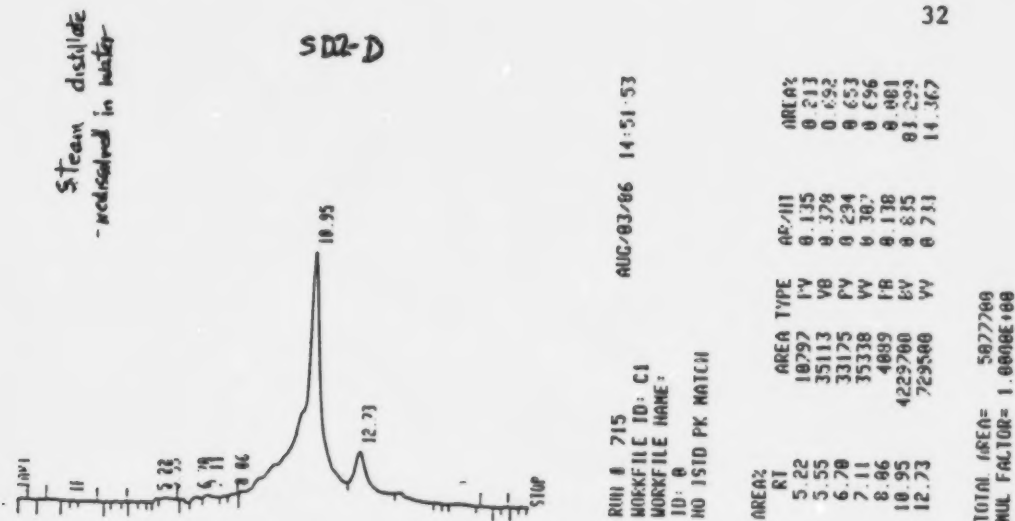
** Should be corrected by a factor equal to the ratio of the response factors for Levogluconan and Methyl Glycol.

Steam was passed through the sample at 2.4 g/min until 250 cm of distillate had been collected. The temperature in the flask remained at 103°C throughout. After vacuum evaporation of the water at 60°C (which entails a small loss of HA) 1.60 g of distillate remained (sample SD2-D). The residue in the flask was 52.3 g indicating that ~14 g of H₂O was accumulated. The analysis of the residue (SE2-R) and distillate are also shown

above. The HPLC traces for the residue and that for the distillate SD2-D are shown below. Analyses are shown above.



It is clear that there has been selective removal of HA and AcOH. Using the mf data on the previous page and the masses used, it may be calculated that of 3.60 g of HA originally present only 0.73 g was removed (20.3%).



In fact the efficiency may not even be as good as this because HA is undoubtedly overestimated in the distillate. There are clearly unresolved shoulders.

The conclusion is that although steam distillation gives very good separation of HA the energy and material efficiency of the process is very low. The HA is recovered in a very dilute aqueous solution which would have to be re-concentrated.

A point which should be noted here is that the residue significantly increased amounts of glucose and fructose and correspondingly less of the peak at 10.53 min. Thus it is almost certain that for this sample, the latter peak is in fact levoglucosan and not methyl glyoxal.

A further point is that the red-brown colour of the residue can be largely removed by treatment with charcoal without inducing any significant changes in the HPLC trace. Similarly, most of the light amber colour of the distillate can be removed by

extraction with methylene chloride in which HA is not soluble. Again this causes no noticeable change in the LC trace.

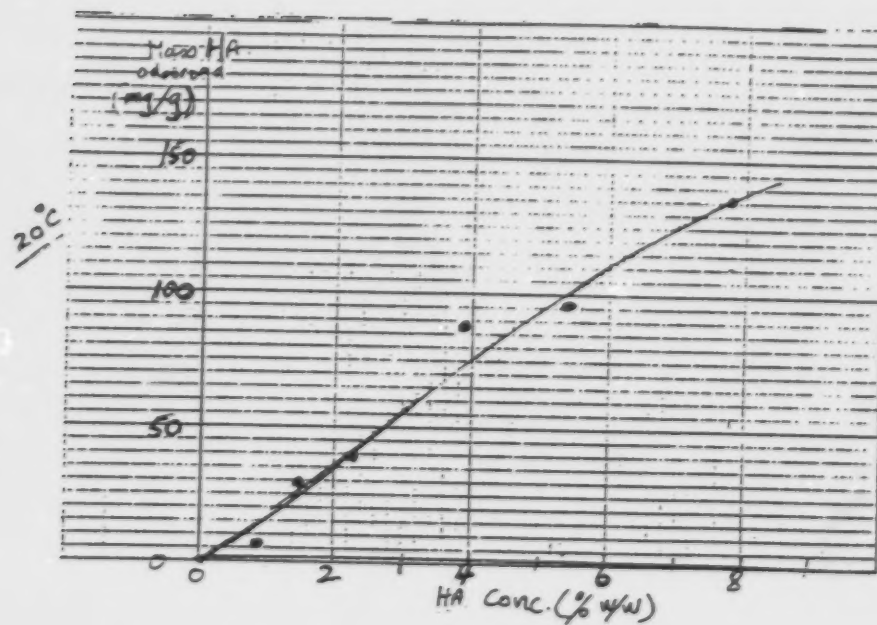
D. Adsorption

The only adsorbent considered here was the hydrophobic small-pore high-silica molecular sieve Silicalite (Union Carbide) [9]. Unlike the majority of aluminated zeolites it has no cationic/acid sites. Consequently it has a positive heat of adsorption for water and only binds organics with the more non-polar ones being adsorbed more strongly. Although HA is polar and so not expected to adsorb very strongly it was felt worthwhile to investigate its adsorption since at the very least the technique might prove to be an energy-efficient way of concentrating dilute aqueous tar extracts. Previous work [10] had shown that ethanol could be selectively removed from aqueous solutions containing glucose which was not adsorbed at all. It was felt that this might therefore also provide a method for removing the troublesome small aldehydes which inhibit fermentation from sugary hydrolysed pyrolysate. (Distribution coefficients and capacities for various substances on silicalite are given in Ref. 11.)

Accordingly a preliminary test on an aqueous tar extract was carried out and this showed a significant ability to remove HA. Acetol was adsorbed especially efficiently.

To estimate capacity an isotherm was constructed for adsorption of pure HA from dilute solutions. Errors are probably a little high as only a small amount (0.7 g) of HA was available for the study. Concentrations were determined by HPLC.

Final HA Conc. % w/w	Amount Adsorbed mg HA/g Silicalite
7.76	135.7
5.36	95.7
3.92	87.5
2.31	38.9
1.50	29.8
0.87	6.7



HA thus does not show the rapid saturation at low concentration characteristic of, say, ethanol adsorption. This is not surprising considering the highly hydrophilic character of HA. Adsorption capacity will therefore be low for very dilute solutions but it still appears useable.

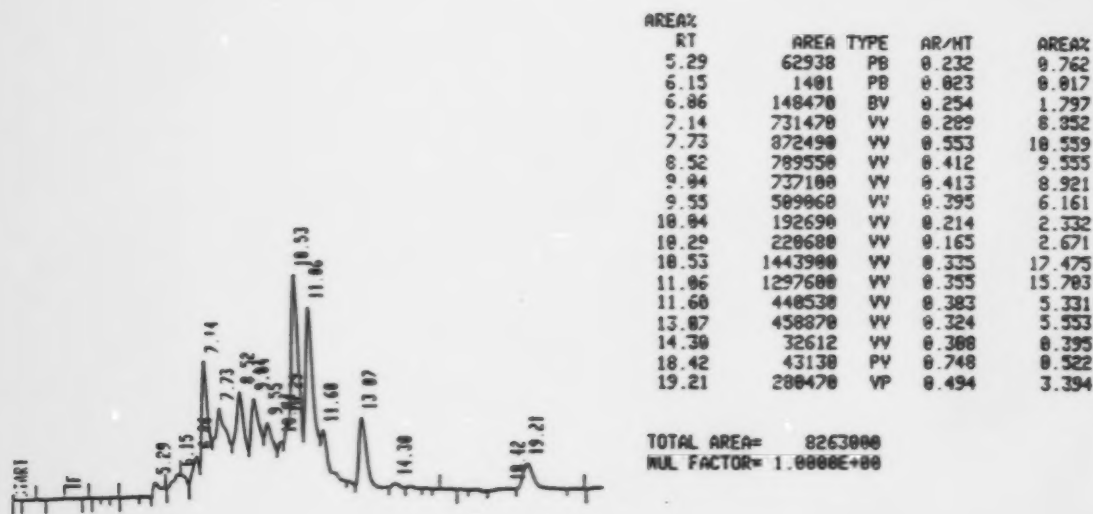
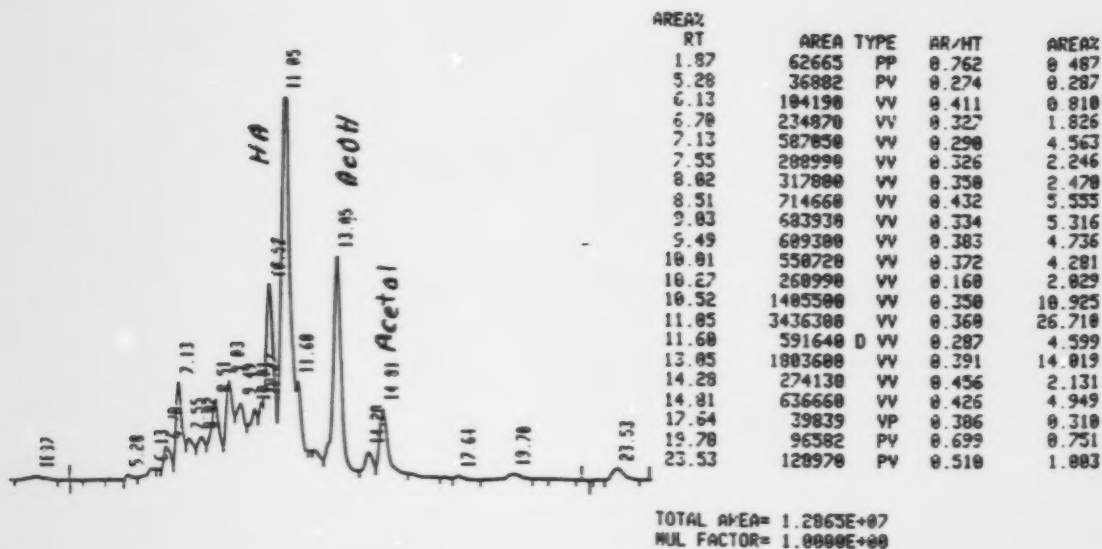
After some preliminary experimentation it was concluded that the best mode of operation would be to start with a dry column, to pass a given volume of the dilute aqueous charcoal-cleaned tar extract over it and to drain it thoroughly. Next the column would be extracted by trickling a fixed volume of the eluting solvent over it. The column would be dried by heating while the solvent would be evaporated from the eluate.

In the initial attempt 10 g of -20 +40 mesh S-115 Silicalite was the adsorbent. 10 cm of an aqueous extract of TL-58 containing about 10% solids was trickled over the adsorbent packed in a 30 cm long column. Acetone was the eluent. A comparison of the HPLC traces for the liquor before and after adsorption shows the expected selectivity for the lower molecular weight compounds (see next page).

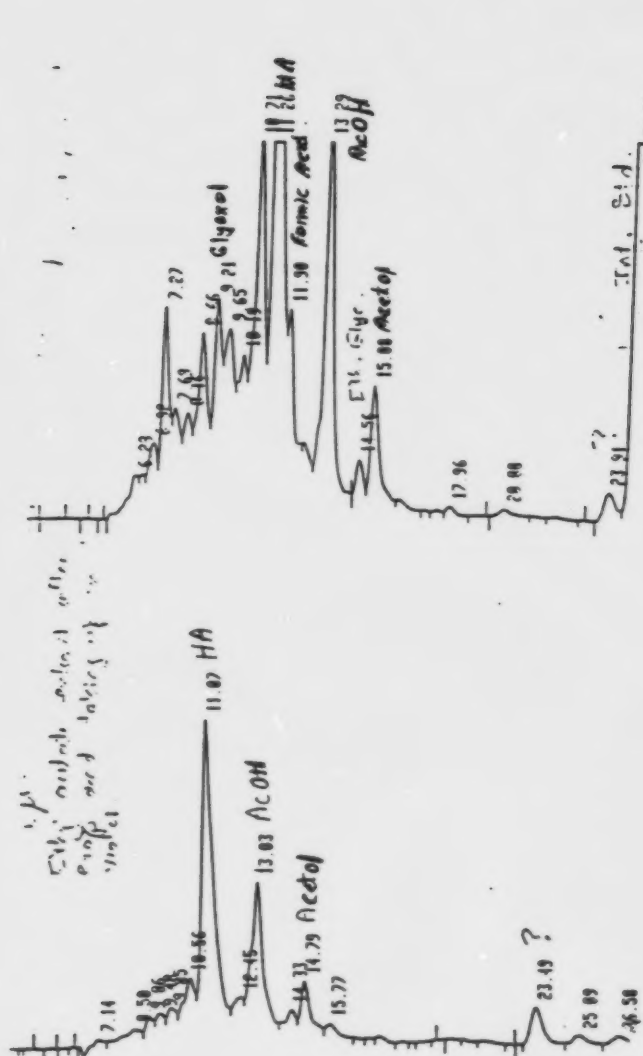
HA adsorption is not complete but is of the order of 70% to 80% (assuming that the peak at 7.13 is not adsorbed at all). The complete adsorption of acetol is noteworthy - indeed the eluate had the characteristic odour of acetol after evaporation of acetone. Acetic acid was also efficiently adsorbed. However

analysis of the eluate after evaporation of acetone showed a significant contamination of the higher molecular weight sugars. In view of the report the glucose is completely non-adsorbed in the internal pores it was felt that this was due to retention of a film of the original aqueous liquor on the outside of the particles. If the eluent was relatively insoluble in water then this film would be displaced as an aqueous phase which could then be separated off. Accordingly the experiment was repeated with water-saturated ethyl acetate as the eluent, but using similar quantities of material (10 cm of eluent were used). A fresh sample of aqueous extract having the analysis shown below was used. This is followed by the HPLC trace for the ethyl acetate extract.

Aqueous extract before adsorption



Aqueous extract after adsorption



RT	AREA	TYPE	CAL #	AMOUNT
6.28	410830	BV		0.411
6.92	560350	VV		0.560
7.27	1377800	VV		1.377
7.69	694920	VV		0.695
8.16	714300	VV		0.714
8.66	1630900	VV		1.630
9.21	1455000	VV	1	0.323
9.63	1518200	VV		1.518
10.19	1207600	VV		1.207
10.71	3342700	VV	2	1.062
11.26	6989200	VV	3R	2.060
11.90	1229800	VV		1.230
13.29	3179600	VB		3.179
14.56	211920	BV		0.212
15.08	823460	VV	4	0.445
17.96	45862	PP		0.046
20.00	86200	BV		0.086
23.91	288090	PV		0.288
24.88	8177800	VB	5S	3.861

TOTAL AREA= 3.3944E+07
 ISTD ANT= 2.3300E-02
 SAMPLE ANT= 6.0350E-01
 MUL FACTOR= 1.0000E+00

Is
Std.
(Propional)

RT	AREA	TYPE	AR/HT	AREA2
7.14	152260	PV	0.481	1.438
8.50	523680	VV	1.088	4.947
9.06	255230	VV	0.349	2.411
9.48	315570	VV	0.398	2.981
9.85	377700	VV	0.422	3.568
10.56	807540	VV	0.548	7.628
11.07	3693000	VV	0.549	34.884
12.45	476260	VV	0.450	4.499
13.03	2029000	VV	0.601	19.166
14.33	433290	VV	0.590	4.093
14.79	682030	VV	0.519	6.443
15.77	258330	VV	0.619	2.440
23.49	392560	VV	0.520	3.706
25.09	103820	VP	0.568	0.981
26.58	86195	I PH	0.561	0.814

TOTAL AREA= 1.0586E+07
 MUL FACTOR= 1.0000E+00

The very good separation of the low molecular weight material is apparent.

A potential advantage of silicalite resides in the fact that it does not absorb microwave energy. This was exploited recently [12] to regenerate a column used to strip ethanol from aqueous solutions.

The possibility of acetalisation of HA by carrying out the reaction in the pores of silicalite has already been mentioned. This possibility is enhanced by the observations above. Highly hydroxylated materials are excluded from the pores. HA and methanol (which would have to be added to the aqueous solution together, possibly, with an organic acid as a catalyst) would be selectively adsorbed. The aqueous phase would be drained off and the adsorbed material driven off by heating.

Finally, the good selectivity indicates that silicalite could also be used in a chromatographic mode.

E. Chromatographic Separation

While liquid chromatography is not usually thought of as a practical large scale method for separation of relatively cheap chemicals, in recent years the chromatographic separation of glucose and fructose using ion-exchange resin columns has been commercialised by a number of firms including Illinois Water Treatment Co. [13]. Most applications have been by the batch mode with its attendant low throughput but progress has also been made using a semi-continuous counter-current mode [13,14]. The adsorption characteristics of this process have also been

studied [15].

An investigation of the literature revealed that HA has been separated analytically on cation-exchange resins in the K⁺ or Na⁺ form from mixtures containing polyols, sugars and simple carbonyl compounds [16]. What is interesting about this is that relatively cheap and common Dowex 50W-X8 resin was effective for this purpose. The eluent was 80% to 90% ethanol in water mixtures. This would be a more favourable solvent than water or aqueous acids from the point of view of the energy cost of removing the solvent.

The mixtures studied [16,17] included compounds like formaldehyde, HA, ethylene glycol, glyceraldehyde, dihydroxyacetone, glucose, fructose, furfural and 5-hydroxymethylfurfural all of which are probably present in the pyrolytic tars. Very interestingly HA eluted before any of these compounds with the exception of formaldehyde. This constitutes a decided advantage for the chromatographic separation of HA by this method since one could operate the column at a high throughput since only a two way split analogous to the glucose/fructose process would be required. This behaviour is in complete contrast to the more complicated action of the HPX-87H resin currently used in our HPLC analyses (c.f. [18]).

A very preliminary investigation of this process was therefore carried out using an extremely short (~ 10 cm) column of -100 +200 mesh Dowex 50W-X8 resin. The column was loaded with a syrup obtained by concentration of the aqueous extract of TL-58 to about 40% solids. (This is similar to the concentrations used in the glucose/fructose process). The eluent was 90% w/w of ethanol in water. In spite of the shortness of the column clear evidence was apparent for the expected mode of action with HA eluting earlier.

It should also be pointed out that particle size exerts a strong influence on the separating power of a column. In the analytical work previously referred to [16], very small mesh (8-14 μ m) resin was used. This leads to very large pressure drops. For production scale activity, large size particles (100-200 μ m) may be used.

The disadvantages of the chromatographic approach are:

(a) energy-intensive preconcentration of the solution may be required; (b) concentration of the eluate is also required; and, (c) capital costs would be high due to the necessary size of the equipment for large throughputs. These are common to the commercial process in which a (presumably) cheaper material, fructose, is isolated. On the other hand eluate concentration should be less energy intensive for HA separation since ethanol is the eluent. The method therefore seems to merit further investigation.

F. Membrane Separation

Membrane separation was not expected to be very selective though their use in the separation of sugars by exploiting differences in permeability under reverse osmotic conditions has at least been investigated [19].

Since a sample of Nafion (Dupont) was available a study was carried out anyway. Nafion is an ion-exchange polymer composed essentially of PTFE with pendant sulfonic acid groups attached. Thus it contains a hydrophobic support with ionic paths through it. Because of the use of PTFE it has great chemical and thermal stability. Indeed it has become the membrane of choice in the chloralkali industry in the few years since its introduction.

The membrane properties described above suggest that it might be selective towards smaller molecules though as mentioned selectivity among the latter was not likely to be great. A cell of simple construction was employed.

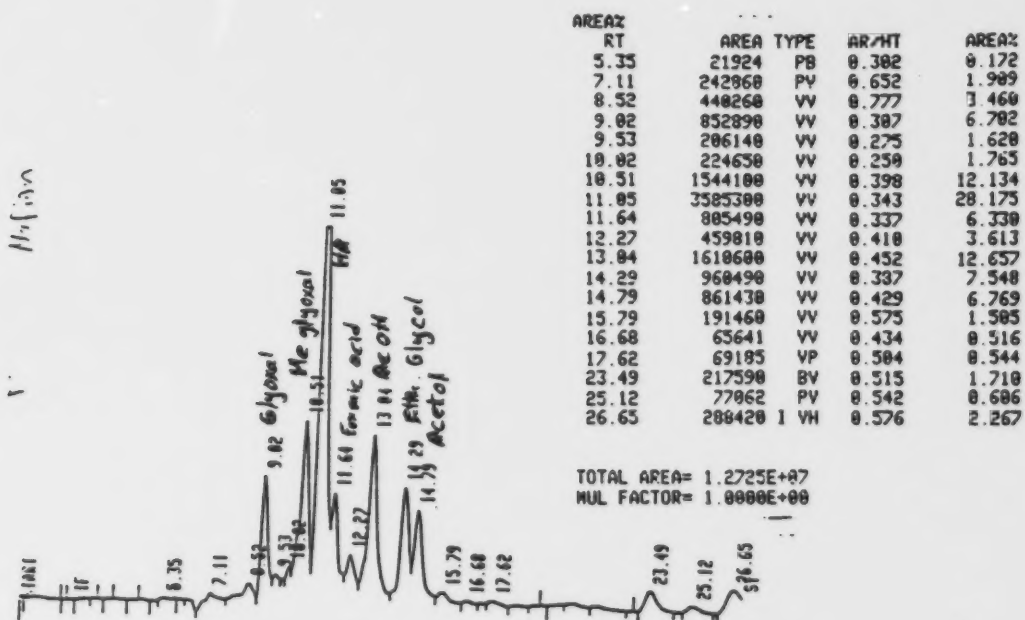
Concentrated "liquid smoke" obtained by slow evaporation of water at room temperature from an aqueous extract of a pyrolysis oil and previously described on p. 6 was charged into a pressurised cell the tip of which was immersed in stirred water. The assembly was left overnight and the water solution was analysed.

The HPLC trace of this solution is shown on the following page.

The expected selectivity to small molecules was exhibited.

While there are apparently some differences in permeability among the various components which passed through the membrane (compare the trace on p. 10) these did not seem large enough to justify more detailed investigation at this stage.

No quantitative estimates of mass-transfer rates were made but they appear "slow".

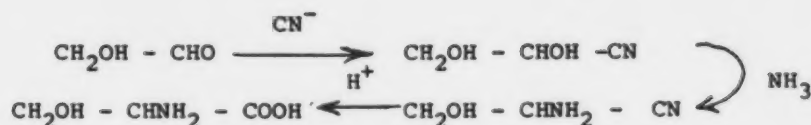


The most likely application for this method would be removal of small inhibitory carbonyl compounds from solutions intended for use as fermentation substrates.

G. Chemical Conversion

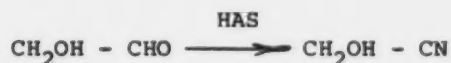
No experimental investigations were made of this possibility but some of the options identified will be very briefly listed below. The success of such a method will depend on identification of a reasonably valuable product which is preferably easier to separate.

- (i) **Ethylene Glycol:** HA is very readily and easily reduced to ethylene glycol by a variety of reducing agents. Whether it would prove much easier to separate is an open question. It at least has the advantage of greater thermal stability.
- (ii) **Glycollic Acid:** Mild oxidizing agents, e.g. Br_2 in water, can oxidize HA to glycollic acid. Separation could be based on its acidic or ionic nature.
- (iii) **D,L-Serine:** HA can be converted to this amino acid in aqueous solutions [20], according to the following scheme.



Separation may be based on either the amino group or the acid properties of the serine.

- (iv) **Glycolonitrile:** Conversion of HA to glycolonitrile can be effected in aqueous solution in high yield using hydroxylamine-O-sulfonic acid ($\text{H}_2\text{N}-\text{O}-\text{SO}_3\text{H}$) as reagent.



The product can be recovered by extraction into ether [21]. No commercial applications of this material were mentioned in the Merck Index.

- (v) **Imidazoles:** These are compounds based on the imidazole ring. Such compounds are formed from HA as well as from other di-carbonyl compounds like glyoxal, pyruvaldehyde (methyl glyoxal) and hydroxypyruvaldehyde (all of which are probably present in the tar) in the presence of aqueous ammonia [22]. The reaction mixture would probably be much too complex to offer any hope of effective product isolation.

A more interesting related idea is the fact that the product of (rapid) initial reaction of HA and ammonia

(viii) Finally attention is drawn to a recent patent (US 4,311,825; Jan. 1982) for the synthesis of water-soluble acetal polymers from hydroxyaldehydes and glycols. In particular HA was specifically mentioned. Such polymers were intended for use as dispersing agents and as reactants in the preparation of polyurethanes. (Note the recent publications of Glasser on the use of polyurethanes as co-polymers with lignin for the formation of binding agents for particle board.

H. Metal Complexes

HA does not seem to be a very suitable agent for formation of chelation complexes. Reference has been found to complexes of levoglucosan with metal hydroxides [Adv. Carbohyd. Chem. 21 (1966) 209; Aust. J. Chem. 12 (1959) 65; J. Org. Chem. 31 (1966) 1845] and to the formation of (soluble) complexes of HA with Tl^{3+} [Pol. J. Chem. 54 (1980) 171]. None of these appear promising.

Conclusions

A number of potential methods for isolation of HA have been identified. At present the most promising approach seems to be adsorption on silicalite. Although acetol and acetic acid are even more effectively adsorbed than HA, it should be relatively simple to purify the mixture, e.g. by extraction with ether or methylene dichloride in both which HA is insoluble but the other two are soluble. Thus acetic acid could be extracted simultaneously.

Reactive extraction as an ester into an organic phase is an interesting possibility worth investigation.

Chromatography and steam distillation will be energy inefficient and are perhaps methods of last resort.

Enough information is not yet available on conversion to other compounds to make a judgement on the matter.

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4.3 Adsorption of Hydroxyacetaldehyde on Silicalite Molecular Sieves

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4.3.1 Prior Work

Adsorption of hydroxyacetaldehyde by hydrophobic silicalite molecular sieves is expected to be a suitable method for separation of this component from pyrolytic tars. Preliminary tests of the adsorption on silicalite SR-115 showed qualitatively a fairly good separation of small molecules in the pyrolysis products; hydroxyacetaldehyde, acetol and acetic acid from carbohydrates.

The first study on adsorption of hydroxyacetaldehyde on silicalite molecular sieves was done by D. Radlein in this laboratory who determined an equilibrium curve in the concentration region 0-8% w/w at room temperature. Distribution ratios reported were in the range 0.7-2.2 at 20°C. The process of adsorption of hydroxyacetaldehyde at a higher temperature (50°C) was also studied in the present work on a column in order to determine the breakthrough point. Further experiments using as a feed a mixture of three main components of tar; hydroxyacetaldehyde, acetol and acetic acid were also planned in a 300 mm long, 30 mm diameter jacketed column.

4.3.2 Liquid-Solid Equilibrium in the System : Hydroxyacetaldehyde-Water-Silicalite Molecular Sieves

Initially, a number of non-flow adsorption measurements were done in order to determine the conditions (temperature) favourable for the process.

Known quantities of hydroxyacetaldehyde, water and molecular sieves were put in contact in closed vials. After two hours or more when equilibrium was supposed to be attained, the concentration of liquid phase was determined by the HPLC method. Amounts of the hydroxyacetaldehyde adsorbed were calculated from the formula:

$$m_{\text{ads}} = m_{\text{init. solution}} \frac{C_{\text{initial}} - C_{\text{final}}}{1 - C_{\text{final}}}$$

where

C = mass fraction of hydroxyacetaldehyde

m = mass of solution and $\begin{cases} \text{initial} & \text{- before adsorption} \\ \text{final} & \text{- in equilibrium} \end{cases}$

The first experiments were done at 50°C. Closed vials containing components of interest were put into the oven for 2 hours and were periodically shaken.

Concentrations of hydroxyacetaldehyde in the samples diminished very significantly. In samples with initial concentration lower than 3%, hydroxyacetaldehyde was not even detected. However, this decrease of the concentration of the liquid phase was not due mainly to adsorption, but to reaction of hydroxy-

acetaldehyde. Chromatograms of solutions showed 6 additional peaks, which suggested that probably condensation (aldolization and autoacetalization) occurred. Therefore, it was decided to carry on further experiments at a lower (room) temperature, but even then the conversion of hydroxyacetaldehyde was observed. It was noticed that solutions in contact with these molecular sieves SR-115 had pH about 10 which could have been the reason for the occurrence of aldol condensation which is known to be catalyzed by OH ions. After adding some HCl to achieve a pH of about 2-3, the conversion of hydroxyacetaldehyde did not occur, even at 50°C so that a number of equilibrium points at $\text{pH} \sim 2$ could be determined. The results are presented in Table 4.3.1 and Figure 4.3.1 and show equilibrium adsorption values about 15% to 30% lower than those reported by D. Radlein, and distribution coefficients within the range 1-1.7.

It should be mentioned that the error in calculation of the amount adsorbed for concentrations of the order of 2% w/w may achieve 25% (assuming $C_f = 0.1\%$ w/w). The one point corresponding to the temperature of 50°C indicates a rather unfavourable influence of higher temperature on the amount of adsorption. On the other hand a promotion of adsorption for smaller sizes of adsorbent particles was observed. The distribution ratio for the fraction -40 +70 mesh was ~ 2.8 while for the fraction -20 +40 mesh ~ 1.5 . The number of experiments was not sufficient to allow a decisive statement on the influence of

temperature and particle size, but results tend to be in agreement with general trends in adsorption equilibrium. Shultz et al. [Talanta 29, 47 (1982)], who did a very extensive study of the adsorption of numerous organic compounds on silicalite molecular sieves, reported very high values of distribution coefficients for many compounds, for example, 100 for acetaldehyde. They used molecular sieves LZ-115 which were heated before use at 750°C for 12 hours. Molecular sieves SR-115 (silica bonded) used in our work were heated at that temperature and became white (before they were more grey), and water in contact with them showed pH $\sim$ 7. However they had lost completely their adsorption properties.

These results suggest that heating destroys the pore structure of SR-115 which is in contradiction with the report of the manufacturer (Union Carbide). The molecular sieves LZ-115 used by Shultz are not produced at present, the corresponding type is now marked SP-115 - silicalite, alumina bonded. This is a material in the form of white pellets and water in contact with it shows pH $\sim$ 7. A series of measurements were performed for that adsorbent in the same manner as described previously for SR-115. The results presented in Table 4.3.1 and Figure 4.3.1 indicate that SP-115 is a better adsorbent for hydroxyacetaldehyde than the SR-115. Distribution coefficients on the SP-115 were in the range of 2 to 3 and no conversion of hydroxyacetaldehyde on their surface was observed.

Table 4.3.1

Liquid-Solid Adsorption Equilibrium in the System:
hydroxyacetaldehyde-water-silicalite molecular sieves

No. of Experim. Sample	% w/w of Hydroxy- acetaldehyde in Liquid Phase	Amount of Hydroxy- acetaldehyde Adsorbed mg/1 g. of Sieves	Remarks
10	2.46	24.7	} SR-115 -20 +40 mesh room temperature
9	3.89	55.1	
8	5.27	87.2	
14	3.60	40.7	50°C
20	3.15	87.8	-40 +70 mesh, 20°C
28	1.90	46.3	} +20 mesh, 20°C
27	4.78	12.6	
30	1.40	34.7	} SP-115 pellets, 20°C
29	3.34	73.2	
34	0.56	8.4	} SP-115 -20 +40 mesh 20°C
32	1.41	9.4	
31	2.05	62.2	
33	3.10	91.0	
35	4.06	91.8	
37	5.96	103.8	
36	7.18	198.4	

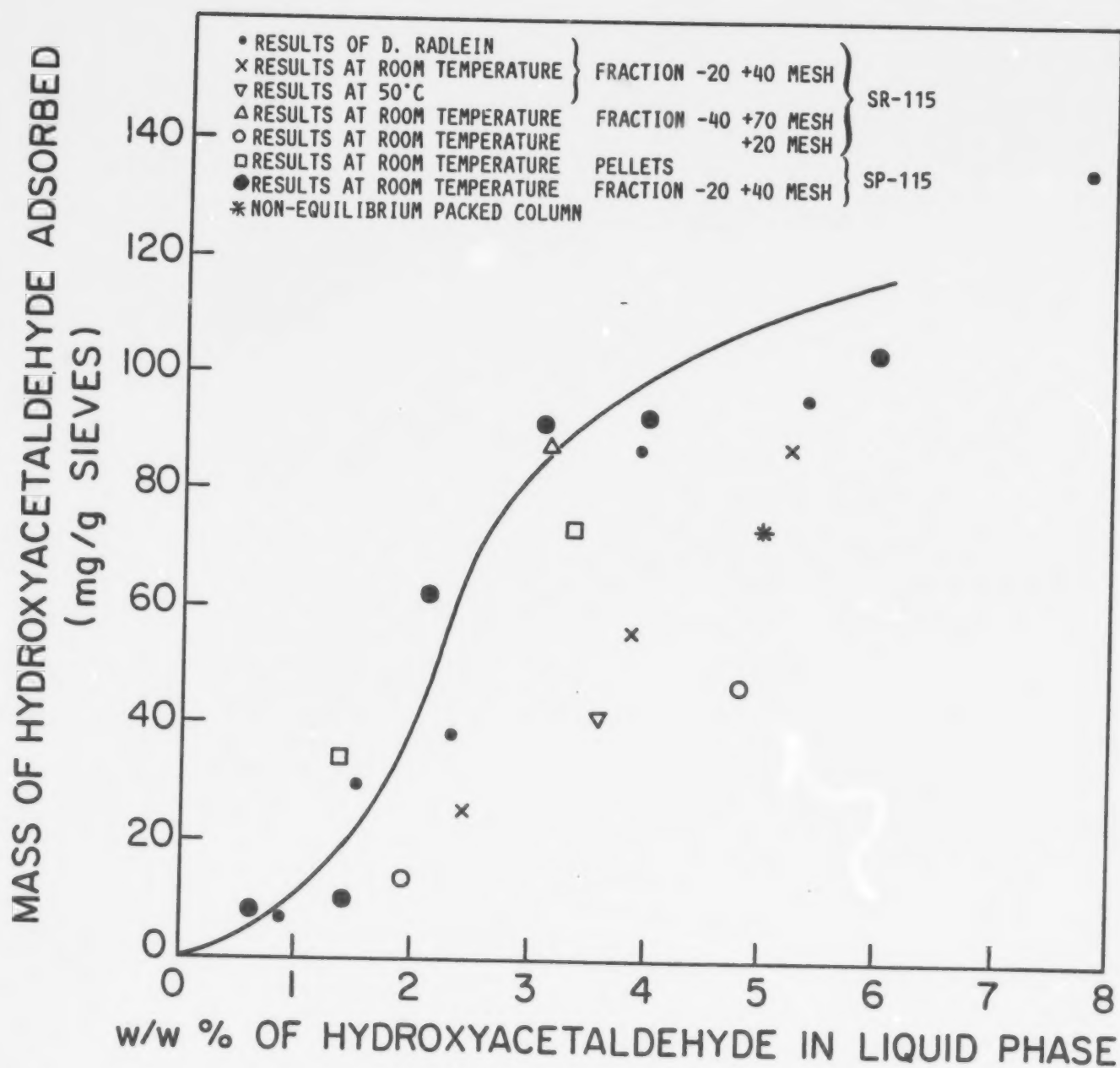


Figure 4.3.1 Equilibrium Adsorption of Hydroxyacetaldehyde
from Water Solution on Silicalite Molecular Sieve

4.3.3 Adsorption in a Fixed Bed Column

The aim of this study was to determine the breakthrough curve for adsorption of hydroxyacetaldehyde from its aqueous solution. For the study a 30 mm inner diameter column was loaded with the -20 +40 mesh fraction of the SP-115. Feed solution contained 5% w/w of hydroxyacetaldehyde.

The column was loaded with a slurry of adsorbent to the height of about 100 mm (higher bed depths would consume more hydroxyacetaldehyde, which is expensive). Feed solution was supplied by an FMI Lab pump at an average rate of 2.7 ml/min. The level of liquid in the column was maintained so that it just covered the bed. Composition of effluent was scanned by a Bio-Rad UV monitor (wavelength 270 nm), and portions were collected and then analyzed by the HPLC method.

Two experiments were done at conditions given in Table 4.3.2. The results are presented in Table 4.3.3 and Figure 4.3.2.

In the first experiment about 40% of the hydroxyacetaldehyde was lost, probably due to conversion occurring in the pores of the adsorbent. Big peaks corresponding to conversion products were detected in the acetone eluate, and the adsorbent bed became yellow after the process. The losses of hydroxyacetaldehyde might have been caused or at least increased by a long residence time of adsorbate in the adsorbent bed, because elution with acetone was done three days after adsorption.

Table 4.3.2

Process Parameters for
Column Adsorption of Hydroxyacetaldehyde

Experiment No.	1	2
Amount of Adsorbent (g)	60	62
Height of Bed (mm)	100.	110.
Flow Rate of Effluent (ml/min)	2.7	2.7
Time of Experiment (min)	51	59
Total Consumption of Solution (ml)	136	145
Hydroxyacetaldehyde Introduced (g)	6.8	7.25
Left in Effluent	1.1	2.2
Eluted with Acetone	3.0	4.45
Lost	2.7	0.6
<u>mg Hydroxyacetaldehyde (1 g sieves)</u>		
Adsorbed and Eluted	50	72
(Calculated by Diff.)	95	82
Volume of Liquid Phase in the Column (ml)	33	33
Mean Residence Time (min)	12	12
Capacity $\frac{\text{mg Hydroxyacetaldehyde}}{\text{g sieves}}$ at 10%	50	35
Breakthrough 50%	87	80

Table 4.3.3

Concentration of Hydroxyacetaldehyde
in the Effluent Leaving the Column,
Inlet conc. 5% weight fraction, 2.7 ml/min

Experiment 1

<u>Time Elapsed min</u>	<u>Volume Eluted ml</u>	<u>Absorbance on the Outlet</u>	<u>% w/w of Hydroxyacetaldehyde on the Outlet</u>
17	45	0.005	0.00
26	70	0.048	0.15
35	95	0.091	0.40
44	120	0.186	1.35
51	140	0.281	2.65

Experiment 2

10	25	0.004	0.00
19	50	0.036	0.14
29	75	0.081	0.35
39	100	0.159	1.10
50	125	0.259	2.30
59	140	0.342	3.50

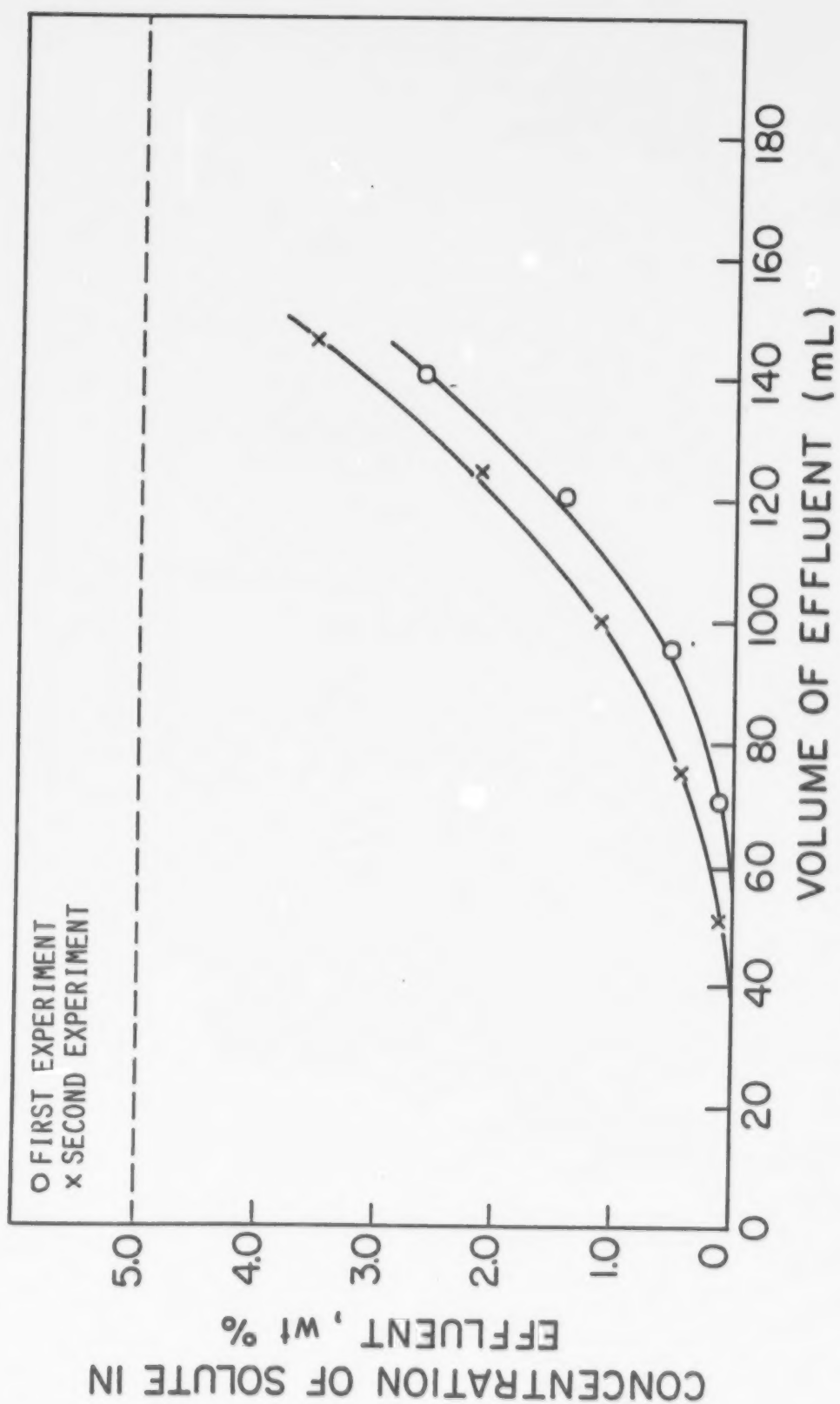


Figure 4.3.2 Breakthrough Curves for Hydroxyacetaldehyde-Water-Silicalite Adsorbent

For the second experiment, elution was carried out without delay after adsorption and loss of hydroxyacetaldehyde was about 8%. No additional peaks were detected in the acetone eluate, but the molecular sieves became slightly yellow however.

Breakthrough curves from the first and the second experiments are slightly shifted one to the other but the second experiment is believed to be more reliable.

During the second experiment, after about 40 min bubbles were formed inside the bed which caused a decrease of effluent rate and disturbed the response of the detector.

Taking into account the amount of hydroxyacetaldehyde adsorbed on molecular sieves and then eluted with acetone during the second experiment, 72 mg of hydroxyacetaldehyde was adsorbed by 1 g of sieves (see Figure 4.3.1).

Additional experiments using regenerated adsorbent and with more careful study of elution of hydroxyacetaldehyde adsorbed were carried out in a subsequent study.

It was noticed that a fraction of hydroxyacetaldehyde remained non-eluted in the bed, probably because condensation reactions occurred in the pores of the adsorbent, which also resulted in reduced adsorption abilities of silicalite SP-115. The aim of the third experiment was to check whether addition of some acid (to $\text{pH} \sim 3$ as in pyrolysis tar) could prevent the condensation reactions. Therefore the solution used as a feed in the third experiment was acidified with acetic acid (0.3% of mass of solution). The experiment was carried out in a manner similar to that reported previously. Its parameters are presented, together with those of the two earlier tests, in Table 4.3.4 and Table 4.3.5, and Figure 4.3.3.

The breakthrough curve for the third experiment is very similar in shape to the former curves. A shift to the right is due to the bigger amount of adsorbent used which involved a bigger volume of liquid retained in the column. In spite of the longer residence time the breakthrough curve for the third test is not steeper than that for the second test, as was expected. Also, the amount of hydroxyacetaldehyde lost (probably by condensation in the pores) is of the same order as in the previous experiment and so is the capacity of adsorbent at 10% of breakthrough. Addition of some acid did not improve the process parameters. The loss of hydroxyacetaldehyde ($\sim 7\%$ of feed) could be accepted provided that it did not involve a decrease of the adsorption properties of the molecular sieves.

Table 4.3.4

Process Parameters for Column Adsorption Tests

Experiment No.	1	2	3
1. Amount of adsorbent [g]	60.	62.	72.
2. Height of bed [mm]	100.	110.	135.
3. Volume of liquid in the bed [ml]	33.		59.
4. Flow rate of feed [ml/min]	2.7	2.7	2.2
5. Mean residence time of solution in the column [min]	12.		27.
6. Duration of experiment [min]	51.	59.	86.
7. Total consumption of solution [ml]	136.	145.	200.
8. Concentration of feed [w/w %]	5.	5.	5.
9. Hydroxyacetaldehyde [g]			
- fed	6.8	7.3	10.0
- left in effluent	1.1	2.2	3.6
- adsorbed and eluted	3.0	4.5	5.7
- lost (by balance)	2.7	0.6	0.7
10. Hydroxyacetaldehyde adsorbed and eluted [mg/1 g sieves]	50.	72.	79.
11. Capacity of adsorbent [mg/g]			
at 10%	50.	35.	35.
of breakthrough 50%	87.	80.	65.

Table 4.3.5

Concentration of Hydroxyacetaldehyde in the Effluent

Experiment #3

Time Elapsed [min]	Volume of Effluent [ml]	Absorbance of Effluent	w/w of HAcAld on the Outlet
32.5	75	0.018	0.00
43.5	100	0.051	0.17
54.5	125	0.114	0.60
65.5	150	0.216	1.63
77.0	175	0.304	3.10
90.0	200	0.346	3.96

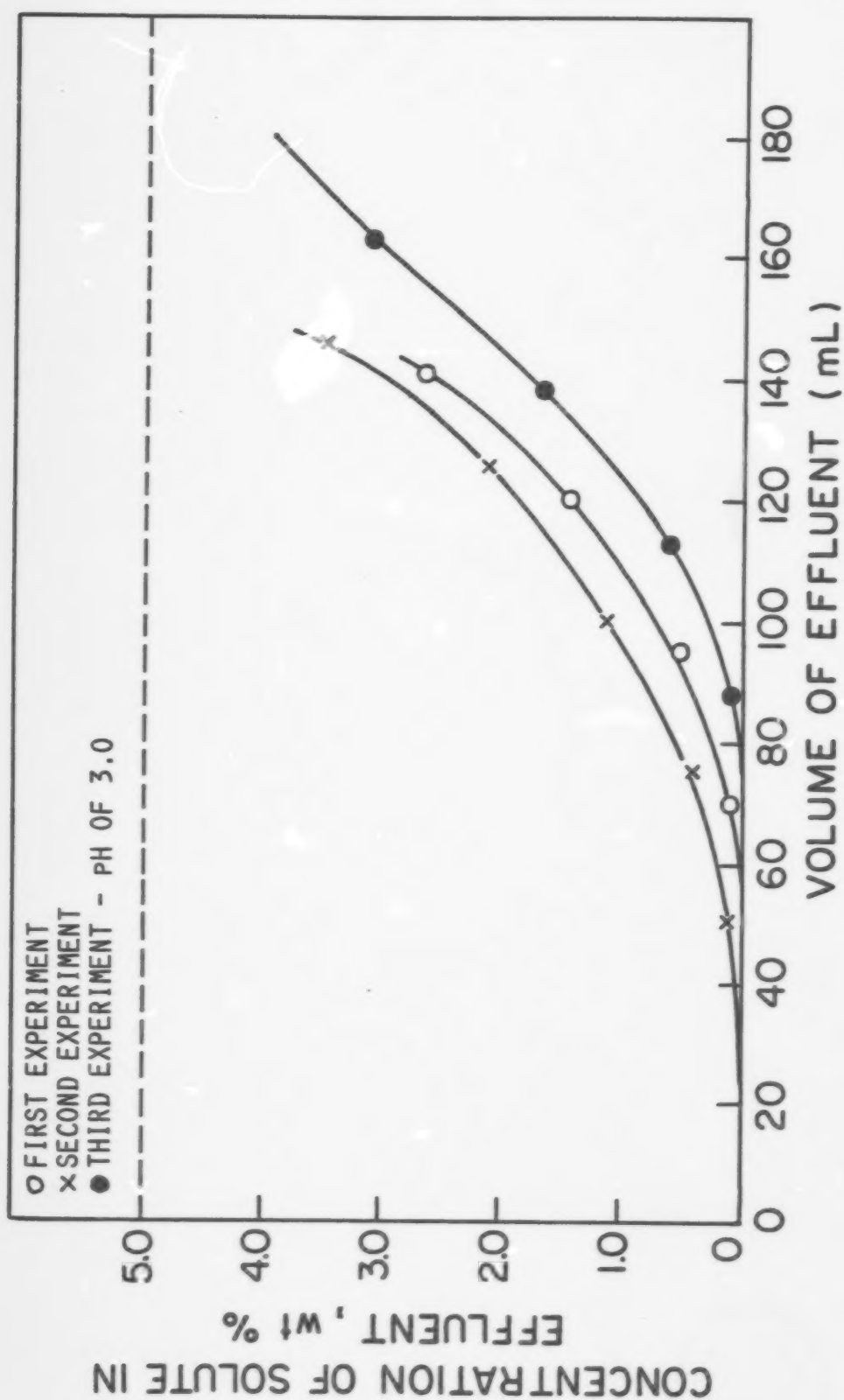


Figure 4.3.3 Breakthrough Curves for Hydroxyacetaldehyde-Water-Silicalite Adsorbent

Therefore, the next stage of the study dealt with the problem of regeneration of the adsorbent used previously.

4.3.4 Regeneration of Molecular Sieves SP-115

Three methods were applied to regenerate molecular sieves used for adsorption and elution with a solvent (ethanol or acetone):

- heating in the oven at 110°C;
- heating in the furnace at 750°C;
- stripping residue with steam and drying in the oven at 110°C.

The regenerated molecular sieves were tested using the static method of adsorption equilibrium measurements reported previously. The results obtained are presented in Figure 4.3.4.

Generally a decrease in adsorption capacity was noticed for regenerated SP-115 in comparison to the fresh solid, especially in the region of higher concentrations of hydroxyacetaldehyde. The steam treatment seemed to be the most efficient in removing the residues from the pores, however, it was not entirely satisfactory. Possibly the results would be better if steam regeneration was followed by heating in the furnace at high temperature.

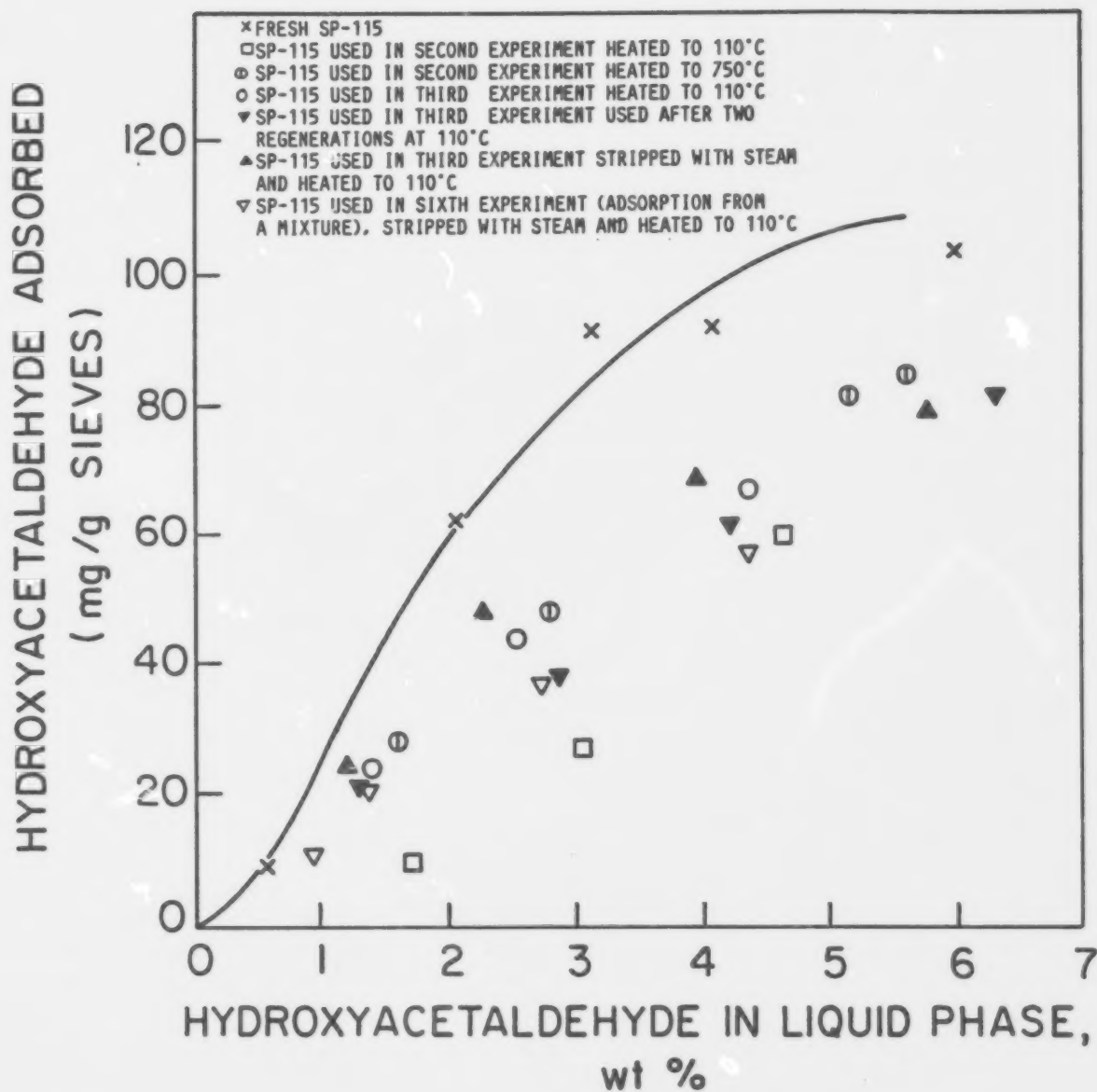


Figure 4.3.4 Equilibrium Adsorption Isotherms for
Hydroxyacetaldehyde-Water-Silicalite
SP-115 Molecular Sieves

4.3.5 Adsorption of Hydroxyacetaldehyde from Tar

Tar TL #58, a product of pyrolysis of poplar wood at 500°C was used in the present study. The tar is a very dark, viscous liquid containing 20% of water.

In this stage of the study tar was separated first by precipitation of the water insoluble lignin fraction. For that reason, an amount of water 2 to 3 times greater than that of tar was added to the tar, which caused the precipitation of lignin. The liquid phase, which was the object of our interest, was decanted from above the dark precipitate. It was a yellow-brownish diluted aqueous solution with water content in the limits 85% to 92% depending on the amount of water added to the tar. The main solutes were hydroxyacetaldehyde, acetic acid, acetol, levoglucosan and other sugars, and some phenolic and furanoic compounds which coloured the solution.

The tar fraction used in experiment #4 was separated using a 2:1 ratio of water to tar. Since precipitation of the water-insoluble part was not complete, the ratio was increased to 2.5:1 in the 5th experiment and to 3:1 in the 6th experiment, which obviously involved a greater dilution of the resulting solutions. Because a strong adsorption of coloured compounds on SP-115 could be expected, the aqueous solutions were first given a charcoal "cleaning" (about 1 g of charcoal per 1 g of solutes) for the solutions used in experiments #4 and #6.

After charcoal treatment, the solutions became pale yellow. However, although charcoal cleaning took out the majority of the coloured components (non-eluted in HPLC analysis), it also took out 30% to 35% of the hydroxyacetaldehyde and other solutes, causing further dilution of the solutions. Therefore, in experiment #5 a non-cleaned solution was tested to compare the results with those solutions which had been treated with charcoal.

Adsorption experiments in the fixed bed column were performed in a similar manner to those for pure hydroxyacetaldehyde solutions. However, UV scanning of effluent compositions was not feasible because of the very strong absorbance of other components in the same range as that suitable for hydroxyacetaldehyde. As in previous experiments, fractions of effluent were collected and analyzed by HPLC. In experiment #4 the column was loaded with a slurry of SP-115, -20 +40 mesh fraction, in experiment #5 with dry adsorbent, -40 +70 mesh fraction, (-70 +100 mesh fraction was first tried but the pressure drop was too high to maintain a flow through the column) and in experiment #6 once more the fraction -10 +40 mesh was used but introduced to the column as a dry bed. The fraction -10 +70 mesh appeared too fine to yield a practical flow rate at normal pressure. The flow rate was very low and was often disturbed during the experiment. After adsorption, the adsorbates were eluted with ethanol (experiment #4)

or acetone (experiments #5 and #6). The process parameters and the results are presented in Table 4.3.6 and Figure 4.3.5.

Breakthrough curves for hydroxyacetaldehyde are flat and stretched, especially for experiment #6, in spite of a lower flow rate than in run #4, probably due to a lower concentration of hydroxyacetaldehyde and to competition from other components (acetic acid, acetol) in occupying adsorbent sites. Eluate was collected in two positions: first, displaced from the column by the solvent, containing besides the main components adsorbed, substantial amounts of sugars which were probably kept in the void volume of the bed, together with a little of the solvent; second (much cleaner for experiments #4 and #6), ethanol or acetone solutions of the three main components with very small amounts of other compounds. However, the eluate is a mixture which must be further treated to recover the hydroxyacetaldehyde.

Removing of acids would seem to be possible using ion exchange resins. Following acid removal, it may be possible to crystallize hydroxyacetaldehyde from acetone solution. Before studying these possibilities, the problem of regeneration of adsorbent needs to be solved. Molecular sieves SP-115 used in these experiments became yellow (experiment #6), yellow-grey (experiment #4) or brown (experiment #5). Neither stripping with steam nor heating in the oven at 150°C restored their original

Table 4.3.6

Process Parameters for Column Adsorption Tests

Experiment No.	4	5	6
1. Amount of adsorbent [g]	61.	86.	62.
2. Height of bed [mm]	125	145-160	110-125
3. Volume of liquid in the bed [ml]		69.	52.
4. Flow rate of feed [ml/min]	2.6	1.0	2.2
5. Mean residence time of solution in the column [min]	20.	69.	24.
6. Duration of experiment [min]	74.	150.	80.
7. Total consumption of solution [g]	175.	150.	185.
8. Composition of feed [w/w %]			
HAcAld	2.28	2.35	1.50
H ₂ O	90.3	85.8	92.9
9. Hydroxyacetaldehyde [g]			
- fed	3.99	3.53	2.78
- left in effluent	2.80	0.44	0.93
- adsorbed and eluted	1.29	1.94	1.83
- lost (by balance)	-	1.15	-
10. Hydroxyacetaldehyde adsorbed and eluted [mg/1 g sieves]	21.	22.	24.
11. Capacity of adsorbent [mg/g]			
at 10%	2	1.1	2.5
of breakthrough 50%			

Feed for experiments #4 and #6 was charcoal cleaned, adsorbent particle size -20 +40 mesh.

Feed for experiment #5 was non cleaned, adsorbent particle size -40 +70 mesh.

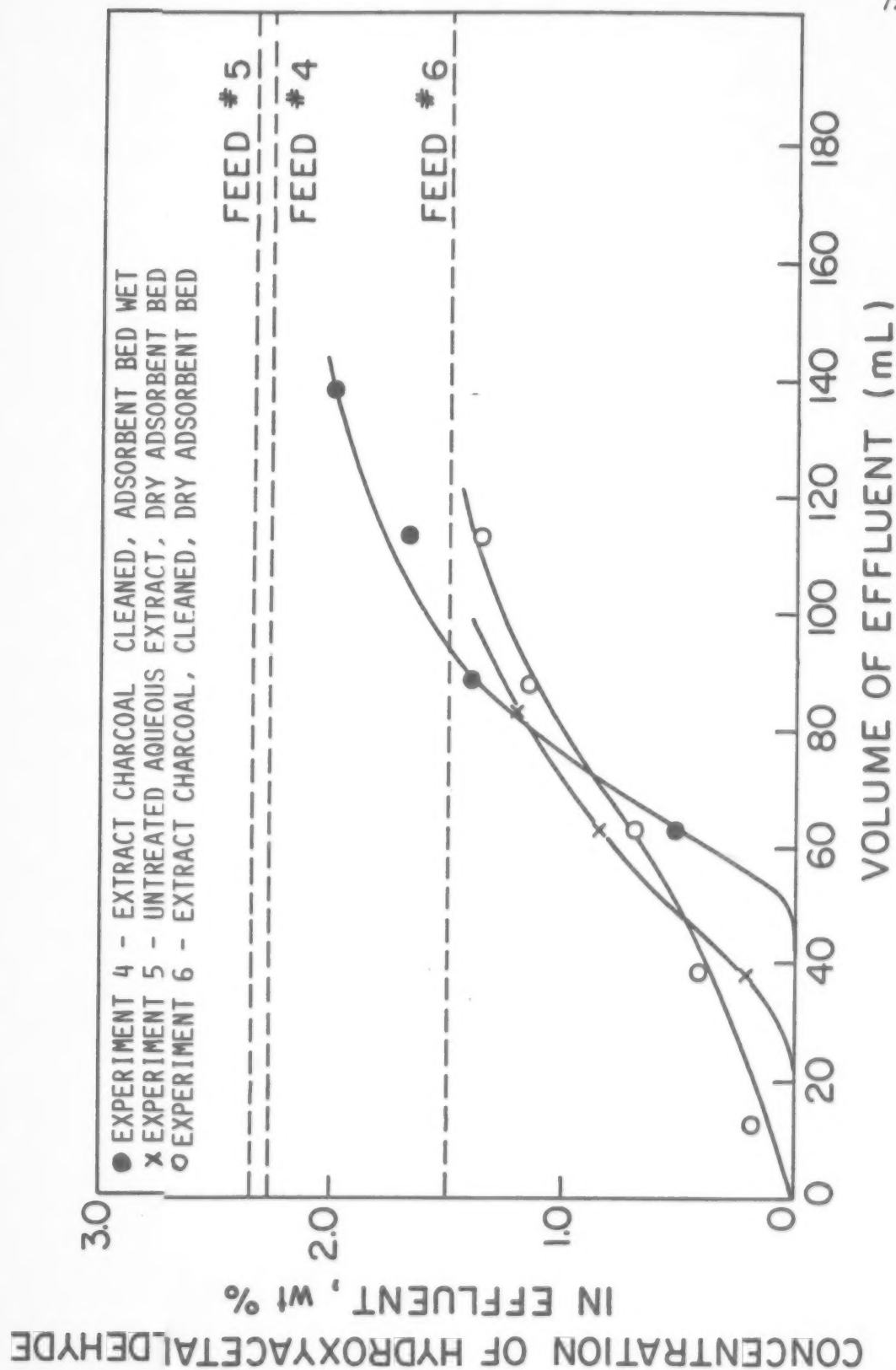


Figure 4.3.5 Breakthrough Curves for Hydroxyacetaldehyde Adsorbed from Aqueous Extract of Pyrolysis Tar

colour and adsorption properties. These results are also presented in Figure 4.3.4. Heating in the furnace at 500°C for four hours did restore the white colour of the adsorbent.

4.4 Extraction of Hydroxyacetaldehyde from Pyrolysis Tar

In parallel to the studies on adsorption, several attempts were made to separate the tar by extraction methods. Knowing that lignin is mainly composed of phenolic type compounds, it was expected that a polar solvent efficient in the extraction of phenol, such as butyl acetate, diisobutylketone or Adogen 364 (trialkyl long chain amine), could separate lignin from sugars and smaller molecular compounds soluble in water, avoiding an excessive dilution involved by the previously described water extraction method.

When butyl acetate was used, two phases were formed but both were very dark and the interface was not visible. The chromatogram of the organic phase showed the presence of acetic acid, formic acid, hydroxyacetaldehyde and sugars, all in smaller amounts than in the aqueous phase which contained substantial quantities of lignin and would therefore require further treatment.

The second phase formed by DIBK or Adogen 364 was much brighter than the aqueous phase and only small amounts of acetic acid passed into the organic phase. The volume of tar stayed

practically unchanged, so this way of removing lignins appeared to be inefficient. Then extraction of small molecular compounds from the tar was also tested using ether. The extraction, which was performed in a Soxhlet apparatus, showed that only about 4% of the tar was soluble in ether. However, the extract was relatively poorer in sugars than the aqueous phase. Nevertheless, the extract composition and low yield do not encourage the application of this method in practice.

After these unsatisfactory attempts at separation of raw tar by extraction methods, further investigations were done using the water soluble tar fraction as a feedstock. It was hoped that a solvent possessing hydroxyl groups could remove hydroxyacetaldehyde from the aqueous solution. First n-butanol was tried, but the distribution ratio of the hydroxyacetaldehyde appeared not to be favorable (about 0.5) and in addition to that compound there were also nearly all the others present in the aqueous phase (probably because of a high water content - 22.5% of the organic phase). Next cyclohexanol, an alcohol much less miscible with water, was tried but the organic phase contained only small quantities of acetic and formic acid, while other components stayed primarily in the aqueous layer.

4.5 Conclusions for Separation Procedures

1. Extractive methods seem to be inefficient for the separation of hydroxyacetaldehyde from pyrolysis tars, or for preferential extraction of lignin from raw tar.
2. It seems that the separation of lignin from tars using water is probably the best first stage of the process. However the optimal amount of water to add to tars for extraction has not yet been precisely established.
3. The present method of charcoal cleaning of the aqueous extract removes 30% of hydroxyacetaldehyde but some degree of treatment seems to be necessary before further treatment of the water soluble tar fraction with a solid adsorbent. Otherwise the coloured components are strongly adsorbed and make both eluate after adsorption and the adsorbent very dark and difficult for further separation or regeneration.
4. Although the adsorption step on molecular sieve SP-115 appeared not to be highly efficient, it could probably be applied to separate sugars from the hydroxyacetaldehyde and to "concentrate" the solution in low molecular weight compounds by less expensive removal of water in comparison to evaporation. However, the problem of the repeated regeneration of adsorbent must be solved before the further recovery steps necessary are studied.

5. Preliminary tests showed that freezing of the water soluble tar fraction after charcoal cleaning resulted in crystallization of water at -3°C . It is worth considering it as a possible method of concentration of the solution. This result also suggests that freeze drying may be a useful method for water removal and tests should also be made using this technique.

4.6 Appendix 1

Definitions -

1. Distribution ratio (coefficient)

$$D = \frac{\text{Amount adsorbed per 1 g of adsorbent}}{\text{Amount in 1 g of solution}}$$

2. Breakpoint (breakthrough point) -

Volume of effluent for which adsorption zone has just reached the bottom of the bed and the concentration of solute in the effluent has risen to an appreciable value (estimated arbitrarily).

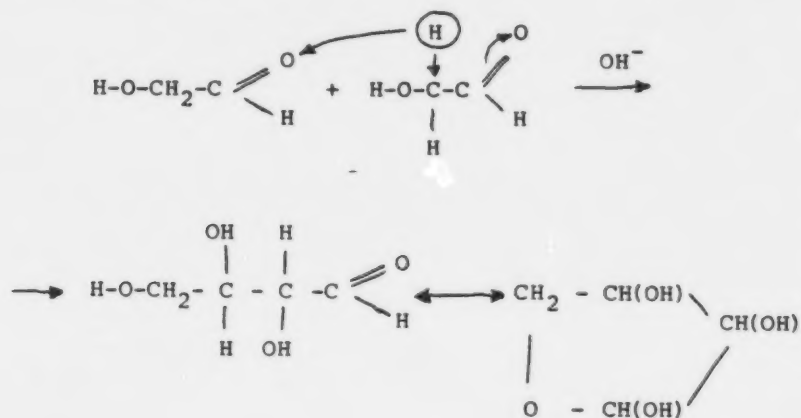
3. Breakthrough curve -

The portion of the effluent concentration curve as a function of the effluent volume between the breakpoint and point where concentration nearly reaches the value corresponding to feed solution.

Appendix 2

Possible reactions of hydroxyacetaldehyde.

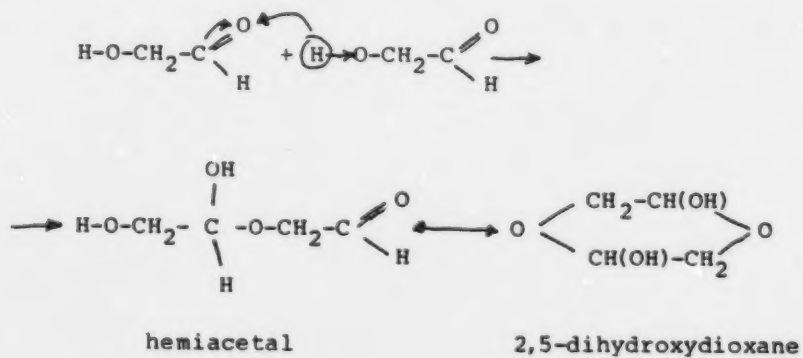
1. Aldol condensation -



erythroze or other carbohydrate (tetroze)

(condensation of 3 molecules can lead to a hexoze)

2. Autoacetalization



4.7 Production of Calcium Acetate from Wood Pyrolysis Tar

Calcium acetate or calcium-magnesium acetate is proposed to replace sodium chloride in de-icing of roads as it is less corrosive to automobiles and structures and less harmful for plants than common salt. Acetic acid is one of the major components of wood pyrolysis tars but its isolation from the tars is more difficult than from fermentation products. However, it might be possible to more readily produce calcium acetate, which probably need not be highly purified for the purpose of de-icing, as one step in the process of utilizing wood pyrolysis products.

For this study the TL #47-pyrolysis product of Brockville poplar was chosen because of its relatively high acid content. It contained 27% of water, 36% of water soluble organic compounds and 37% of water insoluble organics (lignin). The concentration of acetic acid was about 9.5% of tar.

The initial concept was to precipitate calcium acetate (CaAc_2) from the total tar by adding lime. Calcium acetate is easily soluble in water, so an organic solvent had to be added to cause precipitation of the salt. Acetone was chosen as the solvent because of the very low solubility of CaAc_2 in acetone and because its volatility allowed easy recovery.

The solubility of calcium acetate in acetone was determined and was found to be about 1.3 g/1000 g at 20°C, so acetone seemed

to be a good precipitant. An experiment to test the precipitation of calcium acetate by acetone from a pure component mixture was performed. 5.0 g of acetic acid in 45.0 g of water (10% solution) was neutralized with calcium hydroxide, then 70 g of acetone (~60% of the mixture) was added. 6.05 g of white precipitate was obtained which is 91% of the theoretical yield.

Several attempts were then made to precipitate calcium salts of organic acids directly from the pyrolysis tar. Lime was added in small portions to control the pH and with vigorous stirring to a mixture diluted with acetone. Neutralization done in this manner with the range of pH from 3.5 to 7.0 was always accompanied by an abundant precipitation of a brown solid. Though the amounts of this solid changed from one experiment to the other (the results did not show good reproducibility), they were always greater than those calculated from the acid content of the tar. Only a small part of the precipitate was soluble in water and HCl, while the part remaining was soluble in NaOH, resulting in a very dark coloured liquid. This suggests that the precipitate contained considerable amounts of calcium phenates. Chromatographic (HPLC) traces of the water soluble part of the precipitate and of the remaining liquid pyrolysis product indicated that calcium salts of organic acids will precipitate at higher pH values in the region from 7 to 9, but even then they are accompanied by considerable amounts of coprecipitated phenates. Separation of the mixture of phenates

and the acid salts obtained by neutralization at pH values above 7.0 is possible by dissolving the brown solid in water, and evaporation of the filtrate to recover the acid salts. This method does not seem promising however, because of the loss of lignin transformed to phenates and because of the condensation of hydroxyacetaldehyde and other carbonyl components which occurs readily in an alkaline solution.

The second approach was an attempt to precipitate calcium salts from a water soluble tar fraction in order to avoid lignin losses. A water soluble fraction of the wood tar after cleaning by charcoal adsorption and concentration by vacuum evaporation was neutralized with lime in the same manner as previously. The precipitate was brown and was still only partly soluble in water so that a coprecipitation of some other compounds was indicated.

A third approach was to evaporate the acetic acid and formic acid directly under vacuum in order not to degrade the tar by prolonged heating. In addition, only partial acid recovery was desirable because of the need to preserve a low pH in the residual tar to prevent condensation reactions.

The results of experiments with vacuum evaporation are shown in Table 4.7.1.

Table 4.7.1

Process Parameters of Evaporations of Tar

Experiment No.	Temperature of Bath (°C)	Pressure (mm Hg)	Volatiles (w/w %)	Residue (w/w %)	Loss (w/w %)
1	66	40	22.4	68.9	8.7*
2	80	40	34.3	64.6	1.1
3	120	36	39.5	58.5	2.0
4	145	760	35.8	63.4	0.8
4a	145	150	40.4	58.5	1.1

* A large amount was lost due to the lack of a trap on the vacuum line.

The volatile fraction of the tar was analyzed qualitatively by GC/MS and quantitatively by HPLC. Acid content was also determined by potentiometric titration (Sargent-Welch Recording Titrator Model DG), and water concentration was calculated on the basis of Karl-Fischer titration (Metrohm 645 Multidosinate). The composition of residue was determined by HPLC using the same method as for analyses of tars.

The components of the volatile fractions were the same in all experiments but their concentrations varied with the evaporation conditions. The lower the temperature the higher the water content and the lower the acid concentration, except for the temperature of 145°C at which the condensation of tar was very distinctive resulting in the loss of important components and the production of water and water insoluble compounds.

Water content of the collected fraction changed in the range 83% to 67%, acetic acid 12.2% to 16.0%, formic acid 2.5% to 3.2%, acetol 2.7% to 3.7%, methanol 0.6% to 1.3%, hydroxy-acetaldehyde 0.3% to 3.0%. Other components detected by GCMS were: ethanol; methylesters of acetic, propionic, butyric, pentanoic and hexanoic acids; cyclopentanone; 2-cyclopentene-1-one; 2-heptanone; furfural; ethanone-1-(2-furfuryl); phenol and guaiacol. The fractional recovery of acetic acid from the tar changed from one experiment to the other. The results are presented in Table 4.7.2.

Table 4.7.2

Distribution of Acetic Acid between Evaporation Products

Temperature	66°C	80°C	120°C	145°C
Volatiles	27.5*	49.1	67.8	65.7
Residue	42.5	48.8	N.D.	13.3
Lost	30.0	2.1	N.D.	21.0

* less reliable

The most reliable results are those of experiment No. 2 (temperature 80°C) which indicate that about 50% of acetic acid can be evaporated from the tar without losses of other valuable components. At a temperature of 120°C, about 70% of the acid was evaporated, but some undesirable reactions were noticed in

the tar. Probably the optimum temperature of the process would be about 100°C.

Separation by distillation of the volatile fraction of the tar obtained by evaporation was attempted. A small part (~1.6%) boiled under atmospheric pressure in the range 52° to 92°C and had a pale yellow-green colour. It contained most of methanol, ethanol and esters detected in the feed, but no acetic or formic acids. The fraction boiling in the range 97° to 99.5°C (9.5%) was slightly heterogeneous because of the presence of furfural, phenol and guaiacol but its composition was not much different from a subsequent fraction collected within the range 99.5° to 100.5°C (62%) and 100.5° to 104.0°C (20.2%). The last fraction contained less water and more formic acid. About 3% of brown residues, partly insoluble in water, remained in the flask.

Distillation of the aqueous evaporation product did not appear to be a very efficient method of isolation of acids from the tar, but could be used to remove the low boiling and colour compounds.

This two-stage recovery of the volatiles from the tar can be replaced just by direct fractional distillation (under vacuum) of the tar. An experiment was performed under a pressure of about 40 mm Hg, at a temperature of 120°C in the flask. The results are comparable with those obtained by evaporation and

subsequent distillation. The drawback of the process at 120°C is the loss of about 30% of hydroxyacetaldehyde (calculated by balance) as a result of condensation reactions.

The last step of this study was the precipitation of calcium acetate from the volatile fraction of the tar. The reaction was performed in the manner described previously. After having added acetone (70% of mixture) a white precipitate of calcium acetate and calcium formate was obtained with a yield of 95% of that in the volatile fraction (about 64% of the original acetic acid in the tar). No further treatment of the filtrate was done but the recovery of acetone appears to be easy and could be followed by isolation of acetol.

Conclusions

1. The best method of production of calcium acetate from pyrolysis tars seems to be vacuum distillation of the tar followed by the reaction of the volatile acids with lime (or lime-stone) and the precipitation of the acid salts by the addition of acetone.
2. The optimum conditions of the distillation should be established more exactly but it seems that up to the temperature 100°C no undesirable reactions occur in the tar residue. Reducing the pressure to 30 mm Hg (or more) enables the evaporation of more than 50% of acetic acid from the tar and does not appear to involve condensation processes.

3. Further study would be required to confirm the recovery of acetol from the acetone, as well as to evaluate the properties of the acid salt product for de-icing purposes, since it also will contain some calcium formate.
4. If a flash evaporation for the tar could be used in place of a reboiler for the distillation process, probably higher temperatures with higher acid recoveries could be achieved without degradation of the residual tar.
5. Addition of the appropriate stoichiometric amount of magnesium sulfate to the acid salt solution followed by filtration prior to precipitation by acetone would result in the production of calcium magnesium acetate, a compound which already has a market as a de-icer. Magnesium could also be introduced during the neutralization step if desired.

5. PRELIMINARY TESTS OF ADHESIVE PROPERTIES OF PYROLYTIC LIGNIN

5.1 Introduction and Comments on Tests

The poplar lignin produced in the Waterloo Fast Pyrolysis Process was shown in a previous report to be functionally very similar to that produced from steam exploded poplar lignin, except for the absence of alkali in our product, and an apparent somewhat lower average molecular weight. It is easily separated as the insoluble fraction from a water extraction, and after filtering or centrifuging it can be dried to a brown solid which is readily powdered.

A 500 gram powdered sample of pyrolytic lignin of this type, produced as shown in Figure 4.2, was sent to Forintek Canada Ltd. in 1986 for testing as a possible component of the adhesive used for chipboard or plywood. The sample was produced from pilot plant Run 53, carried out at 588°C using a poplar whole tree (bark + wood) feed.

In the next section is the report from Forintek Canada of the tests done with our pyrolytic lignin, using it in two series of tests to replace 70% and 50% of a phenol-formaldehyde commercial adhesive. Results showed that the lignin was

inferior to phenol-formaldehyde but was useable as a component of adhesives but would probably give better results with what was described as "activation".

Our "pyrolytic lignin", especially as prepared in this sample, was a phenolic type of material of relatively low molecular weight. It obviously can act functionally primarily as a replacement for phenol, and would not be expected to be very reactive in self-condensation reactions. By replacing phenol-formaldehyde in the adhesive tests with lignin only, the formulation resulting clearly lost cross-linking capability, and could not be expected to perform at the level of a balanced phenol-formaldehyde resin. It is apparent that further tests should be carried out with the addition of some equivalence of formaldehyde - a procedure which is apparently the "activation" mentioned in the Forintek report. It is our belief that the results of the adhesion tests done by Forintek were remarkably good, considering that the pyrolytic lignin adhesive was not formulated in an optimal way.

On the basis of these results, then, additional tests should be carried out using a more optimal approach to formulation of an adhesive containing our pyrolytic lignin. Because we believe

the pyrolytic lignin is a superior product in comparison to other commercial lignins, proper tests should demonstrate its utility.

5.2 Forintek Canada -
Preliminary Tests of Pyrolytic Lignin as an Adhesive Copolymer

INTRODUCTION

- 1.0 A sample of pyrolysis derived lignin was received from the University of Waterloo for preliminary evaluation as an adhesive copolymer (extender) for waferboard and plywood. The lignin was modified with phenol-formaldehyde following procedures developed by Forintek. The modified adhesives were then employed to prepare laboratory scale waferboard and plywood panels. The experimental panels were evaluated following Canadian Standards Association tests and specifications.

PROCEDURE

2.0 WAFERBOARD ADHESIVE PREPARATION

The lignin as received was found to be a sticky, amorphous, black mass approximately 500 g in weight. The lignin was observed to exude an acrid "tar like" odour.

Methanol was used to dissolve the lignin and to prepare a solution which contained 63% lignin solids. The appropriate amount of commercial phenol-formaldehyde (PF) (Borden chemical W31-54D) at 51% solids was added to a portion of the dissolved lignin to achieve a solution which was in the ratio of 70:30 in terms of lignin to PF based on solid lignin and PF respectively. A second lignin: PF solution was prepared in a similar manner using a 50:50 lignin :PF ratio. The final solids content of both solutions was adjusted to approximately 50% with methanol.

3.0 EXPERIMENTAL WAFERBOARD PRODUCTION

Sufficient Aspen poplar wafer furnish was prepared to produce 4 panels 460 x 460 x 11 mm at a density of approximately 640 Kg/m³. The wafer furnish containing 3.5% moisture was placed in a drum type blender and sprayed with 1.5% of hot slack wax. Following the addition of the wax the experimental lignin: PF adhesive was sprayed onto the tumbling furnish. The adhesive was added at a level of 2.5% solid adhesive with respect to the dry weight of the furnish. The blended furnish was then hand formed onto steel caul plates and the resulting free standing mat was hotpressed at 210°C following normal manufacturing parameters.

Four laboratory waferboard panels were prepared using the 70:30 formulation using press times of 5, 7, 8 and 9 minutes. The 50:50 adhesive was used to prepare duplicate panels with 5 and 7 minutes press times for a total of 4 panels.

The experimental panels were trimmed and cut into test specimens which were conditioned for 1 week at 23°C and 65% RH prior

to testing.

4.0 PLYWOOD ADHESIVE PREPARATION

Lignin:PF formulations were prepared in the ratios 70:30 and 50:50, lignin:PF, respectively, following the same procedure as for the waferboard adhesive. The adhesives were adjusted to a viscosity of approximately 1000 centipoise using methanol.

5.0 EXPERIMENTAL PLYWOOD PRODUCTION

Aspen poplar veneer 3 mm in thickness and equilibrated to an EMC of 6% was employed to prepare 3 ply laboratory plywood panels following the CSA0153-M 1980 standard for poplar plywood. The adhesive was applied using a roller to both face veneers at a level of 40 lb. per 1000 ft² of glueline. The experimental plywood samples were allowed a closed assembly of 15 minutes before hot pressing at 210°C. A total of four 70:30 lignin:PF plywood samples were pressed at 3, 4, 5 and 7 minutes. A similar set of plywood samples were prepared using the 50:50 lignin:PF adhesive.

The experimental plywood samples were trimmed and cut into standard plywood shear specimens as described in CSA 0153-M1980. The specimens were conditioned at 23°C and 65% RH for 1 week prior to testing.

6.0 RESULTS AND DISCUSSION

The waferboard panels were noticeably darker in colour than commercial phenol-formaldehyde (PF) panels and had a distinctive acrid, tar-like odour. The panels were prepared following normal manufacturing techniques and no unusual problems were observed. This preliminary adhesive evaluation was limited to liquids since insufficient material was available for spray drying to powdered resins.

The tests considered to evaluate the experimental waferboards were taken from the Canadian Standards Association (CSA) standard CAN 3-0437.1-M85, Test Methods for Waferboard and Strandboard and CAN 3-0437.0-M85 Waferboard and Strandboard. The tests considered were, breaking strength or, modulus of rupture (MOR), panel stiffness or, modulus of elasticity (MOE), modulus of rupture after 2 hour boil and internal bond, (IB). These tests are essential in preliminary evaluations of waferboard adhesives. The test results for the waferboard specimens are listed in Table 1 and Table 2.

The 70:30 lignin:PF adhesive met the CAN 3-0437.0-M85 requirements for MOR and MOE at the 7, 8 and 9 minute press time, however the waferboards were found to be delaminated at the lower 5

minute press time. None of the specimens were observed to meet the IB requirement.

The 70:30 adhesive appeared to be very slow curing relative to commercial waferboard PF resins which can be fully cured in 3-4 minutes. Declining MOR and MOE values were observed at the longer 9 minute press time probably due in part to heat damage.

The panels prepared with the 50:50 lignin:PF adhesive were limited to 5 and 7 minute press times since these were considered more relevant to compare with commercial PF.

All of the properties of the panels prepared with the 50:50 adhesive were considerably improved when compared to the 70:30 formulation. However none of the specimens were found to meet the IB requirement.

We have included test results for the commercial PF adhesive applied alone (Table 1). These test values form part of a data base which we have been preparing for a new adhesive standard on commercial waferboard adhesives. All new waferboard adhesives will be compared to this data base.

The plywood adhesive formulations did not present any difficulties during the experimental panel preparation. Two plywood shear tests were selected to characterize the bond quality of the plywood. A dry plywood shear test is not a requirement of the standard, however it was selected since it is helpful in establishing the initial bonding capabilities of unknown adhesive systems. The plywood test values are shown in Table 3. The plywood adhesive appeared to be very slow curing as evidenced by the improvement in properties with the longer press times. The 50:50 lignin:PF was observed to perform better than the 70:30 although there was still inconsistency in the bonding as observed at the 5 minute press time. Our experience tells us that shear specimens with high shear loads and poor wood failures indicate that the adhesive is failing to penetrate and bond to the surface wood fibres of the veneer. The high shear load represents the breaking of the glue film itself. Shear loads although a useful research tool are not a requirement of the poplar plywood standard. We have included the test results from a recent evaluation of a commercial PF bonded poplar plywood as a comparison (Table 3).

7.0 COMMENTS AND RECOMMENDATIONS

The lignin sample as received appeared to be rather unreactive for both waferboard and plywood applications.

An activated European lignin sample recently evaluated using similar procedures at our laboratory was found to be significantly more reactive, probably due in part to chemical activation.

Chemical activation of the lignin with some sort of formaldehyde treatment should be considered if future developmental work is contemplated.

Table 1. Mechanical Properties of Laboratory Waferboard Prepared with an Adhesive Containing 70% Lignin and 30% Phenol Formaldehyde.

PRESS TIME (MIN)	AVERAGE DENSITY (Kg/m ³)	MODULUS OF RUPTURE (Mpa)	MODULUS OF ELASTICITY (Gpa)	MODULUS OF RUPTURE AFTER 2 HOUR BOIL (Mpa)	INTERNAL BOND (Kpa)
5	Delaminated	3.5	Delaminated	Delaminated	Delaminated
7	635	18.1	4.07	8.9	142
8	669	16.3	4.36	9.0	126
9	661	21.4	4.19	10.1	116
COMMERCIAL					
PF(W31-54D) 647		33.6	5.25	18.2	552
4 MINUTE PRESS TIME					
CAN3-0437.0-M85					
MINIMUM REQUIREMENT		14.0	2.70	7.0	280

Table 2. Mechanical Properties of Laboratory Waferboard Prepared with an Adhesive Containing 50% Lignin and 50% Phenol Formaldehyde.

PRESS TIME (MIN)	AVERAGE DENSITY (Kg/m ³)	MODULUS OF RUPTURE (Mpa)	MODULUS OF ELASTICITY (Gpa)	MODULUS OF RUPTURE AFTER 2 HOUR BOIL (Mpa)	INTERNAL BOND (Kpa)
5	686	27.0	4.73	12.0	186
7	667	22.7	3.99	14.2	246
CAN 3-0437.0-M85 MINIMUM REQUIREMENT		14.0	2.70	7.0	280

Table 3. Plywood Shear Load Values and Wood Failures for Laboratory Plywood Prepared With 70:30 and 50:50 Lignin:PF Adhesive

PRESS TIME (MIN)	LIGNIN:PF RATIO	AVERAGE DRY SHEAR LOAD (N)	WOOD FAILURE (%)	AVERAGE SHEAR LOAD AFTER BOIL TEST (N)	WOOD FAILURE (%)
3	70:30	600	0	Delaminated	0
4	70:30	802	0	Delaminated	0
5	70:30	972	0	479	3
7	70:30	1500	2	940	0
3	50:50	808	1	260	1
4	50:50	1758	17	1214	75
5	50:50	1510	25	1276	1
7	50:50	1206	11	864	79
COMMERCIAL POPLAR PLYWOOD		N/A	N/A	489	85

CSA 0153-M1980 MINIMUM REQUIREMENT:

- (a) The average wood failure of all specimens is 80% or greater.
- (b) At least 90% of the panels as represented by the test pieces show 60% wood failure or better.
- (c) At least 95% of the panels as represented by the test pieces show 30% failure or better.

University of Waterloo



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May 21, 1986

Waterloo, Ontario, Canada
N2L 3G1

Faculty of Engineering
Department of Chemical Engineering
519/885-1211

Telex Number
069-55259

Mr. Jack Shields
Forintek Canada Ltd.
800 Montreal Road
Ottawa, Ontario
K1G 3Z5

Dear Jack,

Re: Testing of Lignin Sample

Enclosed is a sample (approximately 500 grams) of our lignin produced by a pyrolysis process. This material is solid but softens very readily and will flow at about 40°C.

We have attempted to dissolve this lignin in ammonia solution, but it appears to be only sparingly soluble, rather less than 5%, and possibly only 1% to 2%. However, it is completely soluble in acetone or methanol. Because you mentioned that these solvents were somewhat less desirable for your purpose, we are sending it to you without dissolving it, so that you can dissolve it as you wish.

Although it flows when hot, as you know, it will probably degrade if kept hot for too long a time, since we believe it to be fairly reactive and with a fairly low molecular weight (for a lignin).

The tests we would like done are to assess whether or not this material can be used in wood glues and binders in the same way that commercial lignins are presently utilized. Don Huffman of Ensyn will be discussing the results with you, and is supposed to give us an evaluation.

If you would like additional information please call us.

Sincerely,

Donald S. Scott
Jan Piskorz
(519) 885-1211 Ext 2914 or 4018

c.c. D. Huffman
Ensyn Inc.
275 MacLaren St.
Ottawa, Ont. K2P 0L9

6. FAST PYROLYSIS OF PRETREATED WOOD AND CELLULOSE

6.1 Introduction

Shortly before his death, F. Shafizadeh suggested that pre-treatment of the wood by a mild acid hydrolysis to remove hemicelluloses followed by pyrolysis of the wood would allow a higher yield of fermentable sugars to be obtained, because the pentoses could be recovered from the acid hydrolysate and added to the anhydrosugars customarily formed in wood pyrolysis oils. However, this argument overlooked the fact that very low yields of anhydrosugars are normally obtained from wood except under slow heating at low temperatures (and perhaps vacuum) conditions. Certainly, yields of anhydrosugars and glucose from the rapid pyrolysis of wood in the WFPP are usually less than 5%. However, it was decided in this work, for several reasons, to investigate the effect on pyrolysis yields, and on the composition of the liquid product, of a mild pre-hydrolysis to remove part or most of the pentoses while leaving the cellulose content unaffected.

6.2 Experimental

Samples of a standard poplar wood and of commercial cellulose products (IEA hybrid poplar, SS-144 chromatographic celluloses and Avicel PH-102 microcrystalline cellulose) were used as test materials. Properties of these feeds are given in Table 6.1 as measured in our own laboratory.

Table 6.1

Properties of Feed Materials

Source	Cellulose		Poplar Wood
	Avicel pH 102	Schleicher & Schuell #144 TLC Cellulose Powder	Clean Wood Only Ontario MNR Clone D-38
Moisture, wt%	2.9	4.0	4.6
Ash, % mf	< 0.01%	0.062	0.46
Elemental Analysis, %			
C	44.3	44.4	49.45
H	6.16	6.17	6.05
O	49.5	49.4	44.4
N	Tr	Tr	0.07
Cellulose, % maf	> 99	> 95	49.1
Hemi Cellulose % maf	--	--	20.5
Lignin % maf	--	--	23.5

Pyrolysis of raw and treated wood or cellulose was carried out at standardized conditions for all runs (500°C, 0.46 seconds gas residence time, N₂, -590 μ m particle size) using the bench scale fluidized bed apparatus which has been developed in our laboratories (1). Methods of analysis of tar, gas, char and water yields have also been described previously (2).

Wood or cellulose was hydrolyzed in a batch reactor at 90°C using sulphuric acid concentrations of 1%, 3% and 5% with reaction times of 6 or 19 hours and liquid to solid weight ratios of 4:1 or 12:1. A summary of reaction conditions is given in Table 6.2. Hydrolysis conditions were selected to give a high degree of conversion of the glucuronoxylan, which is the principal component of hardwood hemicellulose, to xylose, while leaving the cellulose unaffected. After treatment, the sample was filtered, washed to a pH of 6.3 and dried at room temperature.

Analysis of the acid hydrolysate and of the water extract of the pyrolysis oils was done by HPLC (Aminex HPX-87H column at 65°C, eluent 0.07 N H₃PO₄, eluent flow rate of 0.32 x 2.25 ml/min).

Table 6.2Hydrolysis Conditions for Wood and Cellulose

Run No.	Residue After Hydrolysis grams*	Acid Conc.	Time hrs.	Temp °C	Liquid: Solid	Xylose Conc.	% of Xylan Removed
A-1 (Wood)	106	5%	6	90	4:1	3.24%	67%
A-3 (Wood)	101.2	1%	19	90	4:1	2.5%	51%
A-4 (Wood)	-150	None	5.5	90	4:1	Tr	Tr
A-5 (SS-144)	-150	5%	5.5	90	4:1	Tr	--
A-6 (Avicel)	-150	5%	5.5	90	4:1	Nil	--

* Initial amount in all tests was 150 grams

6.3 Results

Table 6.2 shows the amount of xylan removed during the various acid treatments. The calculated percent removal is based on an assumed value of 20.5% by weight of pentosans in the IEA poplar (3). The total weight loss from the wood exceeded the equivalent amount of xylose recovered, because of the hydrolysis of some lignin and some minor hemicellulose constituents. The results of Table 6.2 suggest that at even the mildest hydrolysis conditions (1% H_2SO_4 at 90°C for 19 hours at a 4:1 liquid to solid ratio) most of the readily hydrolyzable xylan has been converted to xylose. Changing the liquid to solid ratio from 4:1 to 12:1 at constant acid strength had little effect, indicating the relative completeness of the initial hydrolysis reactions of hemicellulose. Also shown in Table 6.2 are the blank run carried out using hot water only, as well as the conditions for the acid treatment of the commercial celluloses used.

The results of the pyrolysis runs for the untreated and treated poplar wood are given in Table 6.3. The two runs in which most of the xylan was removed by acid hydrolysis gave a 78% to 80% yield of organic liquid, and a greatly reduced yield of water. The char and gas yields were also reduced to about one half the value of that for the untreated wood. Table 6.4 gives the analyses of the organic liquid fraction produced in the pyrolysis runs shown in Table 6.3. The most notable feature is the

Table 6.3

Pyrolysis of Raw and Treated Wood

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Overall Product Yields

	PP 59	A - 2	A - 4	A - 3	A - 1
Feed	Poplar Wood Pilot Plant	Poplar Wood Bench Unit	Wood Hot H ₂ O ext.	Wood Very Mild Hyd.	Wood Mild Hyd.
Feed Rate, gm/hr	3,390	29.6	33.4	16.2	21.9
Temp °C	504	497	504	503	501
Vapor Res. Time, s	0.48	0.46	0.46	0.46	0.45
Particle Size, μ m	-1000	-590	-590	-590	-590
Moisture, %	4.6	3.3	7.0	0.83	16.5
Cellulose, %	49.1	49.1	50.0	63.4	62.8
Yields, % Wood mf					
Organic Liquid	66.2	65.8	69.8	78.3	79.6
Water	10.8	12.2	7.6	5.0	0.9
Char	11.8	7.7	9.3	6.0	6.7
Gas	11.0	10.8	12.3	7.7	6.4
	99.8	96.5	99.3	97.0	93.6

Pyrolysis of Raw and Treated Wood
Analyses of Liquid Product

	<u>PP 59</u>	<u>A-2</u>	<u>A-4</u>	<u>A-3</u>	<u>A-1</u>
Yields of Tar Components % mf Feed					
Oligiosaccharides		0.7	2.58	3.80	1.19
Cellobiosan		1.3	3.18	10.08	5.68
Glucose		0.4	1.0	1.67	1.89
Fructose		1.31	2.35	4.00	3.89
Glyoxal		2.18	3.68	4.10	0.11
1,6 Anh. Glucofuranose		2.43	4.12	3.08	4.50
Levoglucofan		3.04	5.17	15.7	30.42
Hydroxyacetaldehyde	8.86	10.03	12.61	5.35	0.37
Formic Acid		3.09	3.42	2.54	1.42
Acetic Acid	4.33	5.43	5.20	1.46	0.17
Ethylene Glycol		1.05	0.78	0.43	-
Acetol	2.93	1.40	1.20	0.06	0.06
Methylglyoxal		0.65	1.28	0.41	0.38
Formaldehyde		1.16	1.78	0.72	0.8
Aromatics (lignin)	↑ by G.C.	16.2	-	18.0	19.0
Totals		51.5	-	71.4	69.9
% of Pyrolysis Oil		78.3	-	91.2	87.8
Sugars		9.2	18.4	38.3	47.6
Cellulose Content					62.0

sharp increase in levoglucosan and in total sugar content of the oils from the acid hydrolyzed wood, while a sharply reduced yield of hydroxyacetaldehyde occurred simultaneously. A marked decrease in the amounts of acid produced from treated wood is also apparent.

Similar results are shown in Table 6.5 for a commercial low ash cellulose (SS-144) which gave high yields of hydroxyacetaldehyde from pyrolysis at 500°C, and much less levoglucosan. After a mild hydrolysis, levoglucosan yield was sharply increased, and that of hydroxyacetaldehyde decreased. A large increase in cellobiosan yield was also observed for both this cellulose and for the treated wood.

Results for the pyrolysis of untreated and for acid washed Avicel PH-102 are also given in Table 6.5. Again, a large increase in levoglucosan yield and an almost zero yield of hydroxyacetaldehyde result from acid washing. The yields of acids and of other minor constituents is also sharply decreased for the acid washed Avicel, although cellobiosan yield increases.

The hydrolysate liquors from wood were analyzed for Ca, Mg, Na and K contents, which were compared to those found from analysis of the ash from the untreated wood. Essentially all these cations were removed in the acid treating step. According to our analyses, the wood sample used for these tests contained about 1300 ppm Ca, 1800 ppm K and 40 ppm Na, maf-basis.

Table 6.5

Pyrolytic Products from Celluloses

Run Source	SS-12 Commercial SS 144	A-5 Treated SS 144	6 Avicel pH-102	A-6 Treated Avicel
Temp °C	500	502	500	503
Yields, % mf of feed				
Organic liquid	72.5	83.5	87.1	86.3
Water	10.8	6.1	3.1	?
Char	5.4	1.3	2.5	5.7
Gas	7.8	3.9	8.9	3.3
Hydroxyacetaldehyde	15.3	6.2	8.6	0.43
Levoglucozan	7.0	31.8	26.9	38.41
Cellobiosan	4.0	11.5	10.1	5.6
Glucose	1.0	1.8	2.1	2.0
Fructose	2.0	3.0	4.7	2.7
Glyoxal	3.5	5.5	6.5	2.1
Methylglyoxal	0.8	1.3	0.23	0.30
Formic Acid	5.5	1.9	3.8	1.5
Acetic Acid	4.9	0.1	1.4	0.03
Ethyleneglycol	1.7	0.02	0.56	0.00
Formaldehyde	1.2	0.94	0.72	0.24
Acetol	2.2	0.12	0.04	0.02
Anhydroglucofuranose		5.5		7.0
Oligosaccharides		5.3		
% of Oil Quantified		89.6		

6.4 Discussion

The reason for the great increase in levoglucosan and the parallel decrease in hydroxyacetaldehyde yield following acid treatment is not clear from these results. It is tempting to say that the change in product distribution is due to the removal of inorganic cations during the acid treating process, since it is known that these cations can catalyze the decomposition of cellulose and its degradation products. However, the low ash content SS-144 cellulose also showed this remarkable increase in levoglucosan yield. Also a comparison of results for the untreated and the acid washed Avicel PH-102 microcrystalline cellulose (average ash content 40 ppm) also shows an increase in levoglucosan yield from 27.0% to 38.4% of the feed when pyrolyzed at 500°C while hydroxyacetaldehyde and cellobiosan decrease from 8.6% to 0.43% and 10.1% to 5.6% respectively.

While there is little doubt that the content of inorganic cations affects the product distribution, it appears that it is not the only effect, and the morphology and degree of hydrogen bonding in the cellulose must also influence the composition of the pyrolytic liquids. The extent of degradation of the cellulose as measured by the degree of polymerization (DP) was not measured for these samples, but this factor should also be evaluated.

Apparently, the xylan content of wood is a primary source of much of the water, gas and char formed in fast pyrolysis, as well as being a major contributor to the acid content of the pyrolytic oils.

When the results of Tables 6.3 and 6.4 are recalculated on the basis of cellulose content, then it is found that fast pyrolysis of the acid treated wood can convert 75% of the cellulose to sugars - largely anhydrosugars, with 15% reducing sugars and 15% disaccharides. When the pentose content of the acid hydrolysate is added to this, a high conversion of the wood to sugars is obtained, with about 80% of the holocellulose content yielding sugars of various kinds. Fast pyrolysis of acid treated wood may well be an economical route for the production of fermentable sugars, as Professor Shafizadeh suggested (4).

It is also of interest to note that for the wood samples and for the SS-144 cellulose, there is an almost exact molal correspondence between the changes in levoglucosan yield and the changes in hydroxyacetaldehyde yield. These results appear to confirm the hypothesis published recently by us (5) that in fast pyrolysis, the decomposition of one mole of levoglucosan yields one mole of hydroxyacetaldehyde, at least in the case of native celluloses. However, since that publication, we now believe that cellulose decomposes by several parallel pathways,

with the formation of levoglucosan or of hydroxyacetaldehyde being two of the most significant. Analysis of the variation of yields with temperature from Avicel by Halling (6) has given strong support to this postulate. The production of hydroxyacetaldehyde and levoglucosan in parallel processes has also been proposed recently by Richards (7) (see also Figure 6.1), in agreement with our more recent results. However, the reaction conditions necessary to favour the one pathway over the other are not yet clearly established nor understood, and further work is currently underway in our laboratories to explore this mechanism.

The yield of hexoses from cellulose in the best case shown for wood in Tables 6.3 and 6.4 is 93%. In fact, the cellulose in wood (cellulose I) apparently is more quantitatively converted to monosaccharides and disaccharides by fast pyrolysis than is secondary or crystalline cellulose. The fast pyrolysis process may well be the best present method to obtain high yields of fermentable sugars from cellulose by a simple economical process. Further, the resulting aqueous fraction, after removal of the lignin-derived fraction, and hydrolysis of the anhydrosugars, would have a reducing sugar content of 200 to 250 gm/l, and could have a further pentose content of 50 to 90 gm/l, much higher than most existing processes for saccharification of cellulose.

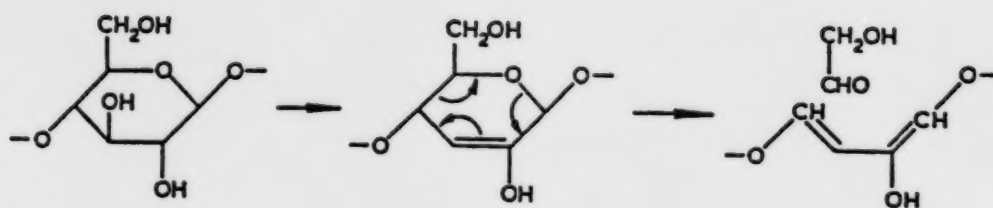


Figure 6.1 Proposed Mechanism of Production of Hydroxyacetaldehyde from Cellulose [from Richards (7)]

6.5 Pyrolysis of Pretreated Wood from St. Lawrence Reactors Ltd.

In the work reported in the preceding sections a highly specific conversion of cellulose to levoglucosan and other sugars was achieved in the WFPP by using wood given a mild acid pretreatment (5% H_2SO_4 at 90°C for 6 hours). No attempt has been made to optimize the pretreatment process. Therefore, it was of interest to determine the effect on yields of pyrolytic sugars of a different wood pretreatment particularly one from a potentially commercial process. Accordingly, samples of pretreated wood were obtained from St. Lawrence Reactors, prepared by their continuous plug flow short time, high temperature HCl prehydrolysis method (0.5% HCl for 6 minutes at 165°C). A pyrolysis test on this material was disappointing in terms of yields of sugars, although an 81.3% yield of liquid was obtained. However, their sample was washed extensively with plant water, which could add calcium or sodium ions back to the acid treated wood. Therefore, a pyrolysis test was repeated using St. Lawrence Reactors' pretreated wood which had been previously washed at room temperature with 0.36% HCl to remove adsorbed cations. Levoglucosan yield was tripled, and other sugars also increased, with identified sugars going from 20% to 47% of the solids content of the aqueous phase (only 60% of the total aqueous phase solids were identified). However, sugar yields did not approach those shown in Table 6.4.

It appears that the prehydrolyzed wood as presently prepared by St. Lawrence Reactors is not optimal for sugar production by the WFPP. Further tests should be done with wood which has been given more or less acid treatment or reaction time to establish the best procedure for short time, high temperature pretreatment. Very good results have already been obtained by us with low temperature, longer time, treatment. It is also possible that pretreatment with SO_2 solution (as done by M. Wayman) may be a suitable technique for the WFPP.

The disappointing results obtained with the SLR pretreated wood led to a decision not to use this feedstock (which was available in adequate quantities) for a pilot plant test. As a result, the original plan to conduct a larger scale pyrolysis run with pretreated wood was not carried out, and instead a number of bench scale runs, as described above, were done with the SRL wood.

6.6 References

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- (6) Halling, J., Modelling the Liquid Product Distribution from the Waterloo Fast Pyrolysis Process MASc Thesis, Dept. of Chemical Engineering, University of Waterloo, August, 1987
- (7) Richards, G.N., J.Anal.Appl.Pyrol. 10, 251-256, 1987

7. DESIGN OF A MOBILE PROCESS DEMONSTRATION UNIT (PDU) FOR THE WFPP

7.1 Introduction

The original contract objectives allowed for an optional task, that is, to sub-contract for a mobile PDU design, or to carry out further pilot plant experimentation. It was concluded during the course of the contract work and after consultation with the Scientific Authority (Dr. D. Fung) that it would be more advisable to have a design ready if serious industrial interest in the Waterloo Fast Pyrolysis Process was to be cultivated. Accordingly, a sub-contract for the design was given to BBC Engineering (John Black, President) who had also carried out the preliminary economic feasibility study in 1985 for a full scale plant based on the WFPP. The final report, with modifications was accepted in October, 1987.

The Summary of the BBC Engineering report is given in Section 7.2, and the basis of the design with some detailed results is given in Section 7.3. The detailed equipment specifications together with the various layout drawings and flowsheets are attached to this report as Appendix 2.

7.2 Summary

The preliminary design of a trailer mounted plant, based on the Waterloo Fast Pyrolysis Process, has been completed.

The entire process, which includes intermediate storage, shredding, drying and pyrolysis, can be mounted on a single low-boy trailer, 12 m long x 2.44 m wide. The system, which does not require any site erection, can be operated by two people, one of whom is required to load biomass into the storage bin on a batchwise basis, once every hour. The other operator is required to monitor the process.

The plant includes sufficient automatic control to ensure safe, stable operation. Also provided are instruments that will measure the data needed for complete mass and energy balances. Additional instrumentation is included to monitor the performance of ancillary equipment for later scale-up. Information will be processed through a data acquisition system to an IBM-PC based computer and can be formatted and analyzed through a conventional spreadsheet program.

The complete system will cost around \$926,000.00 and requires only hook-up of cooling water and electricity.

7.3 Detailed Description of Design

Final

DESIGN FOR A
MOBILE PYROLYSIS DEMONSTRATION PLANT

Prepared for
THE UNIVERSITY OF WATERLOO

By
BBC ENGINEERING & RESEARCH LTD.
Markham, Ontario

October 1987

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- WA-1 Process Flow Diagram
- WA-2 Single Line Electrical Schematic
- WA-3 Preliminary Instrumentation Drawing
- WA-4 Simplified Equipment Layout

DESIGN FOR A MOBILE PYROLYSIS DEMONSTRATION PLANT

1.0 INTRODUCTION

Research into a novel pyrolysis process, carried out at the University of Waterloo by Professor Scott and J. Piskorz (1984), has resulted in the successful testing of a small pilot system. To assist in scale-up and marketing of the technology, it has been proposed that a mobile (200 B.D. Kg/hr) demonstration facility be constructed.

It is intended that this unit would be transported to preselected locations where different types of waste are available. Tests could then be carried out, on site, to identify and resolve problems associated with these different feed materials. The operating parameters would be collected by a data acquisition system and the properties of the various products, liquid, gas and char, would be measured.

The mobile facility would serve a threefold purpose:

- . Permit scale-up parameters to be evaluated.
- . Provide operating data for different types of waste.
- . Demonstrate to plant owners that their wastes could be successfully converted to useful energy products which, in turn, could be utilised at the site or sold to other users.

The philosophy for design of the mobile unit is that it be a trailer mounted plant with little or no requirements for field assembly, other than utility hook-up for electricity and cooling water. Liquid and char products would be collected in 55 gallon drums for testing or disposal while the gas would be flared. For simplicity in start-up and operation, all fuel requirements for the unit would be provided by propane. - In a conventional commercial system, the energy for drying and pyrolysis would, of course, be provided from the products, particularly the gas and char.

It is intended that the facility would primarily be operated in single 8 hour shifts with the option of going to 24 hour operation for short periods of time.

BBC ENGINEERING & RESEARCH LTD. was asked to provide support engineering to the group at the University of Waterloo for the design of the facility.

2.0 PROCESS DESCRIPTION

The biomass pyrolysis liquefaction process described herein, was invented and developed by Professor D.S. Scott and J. Piskorz at the University of Waterloo. The process is described in a variety of publications including Scott (1983), Scott (1984) and is shown in figure 2-1. This basic flow diagram was modified slightly to include materials handling and storage, drying and product collection (Drawing WA-1).

The process, which has a design capacity of 200 Kg/hr, is divided into four major operating areas:

- . Loading of material by a pneumatic conveyor into an intermediate storage bin - area 100.
- . Grinding and drying of the feedstock followed by conveyance into a surge bin - area 200.
- . Pyrolyses and separation of the product - area 300.
- . Collection and disposal of the product - area 400.

In addition to the process areas, there are two other modules, auxiliary services and instrumentation. The latter also includes data acquisition.

Each of these modules is described separately.

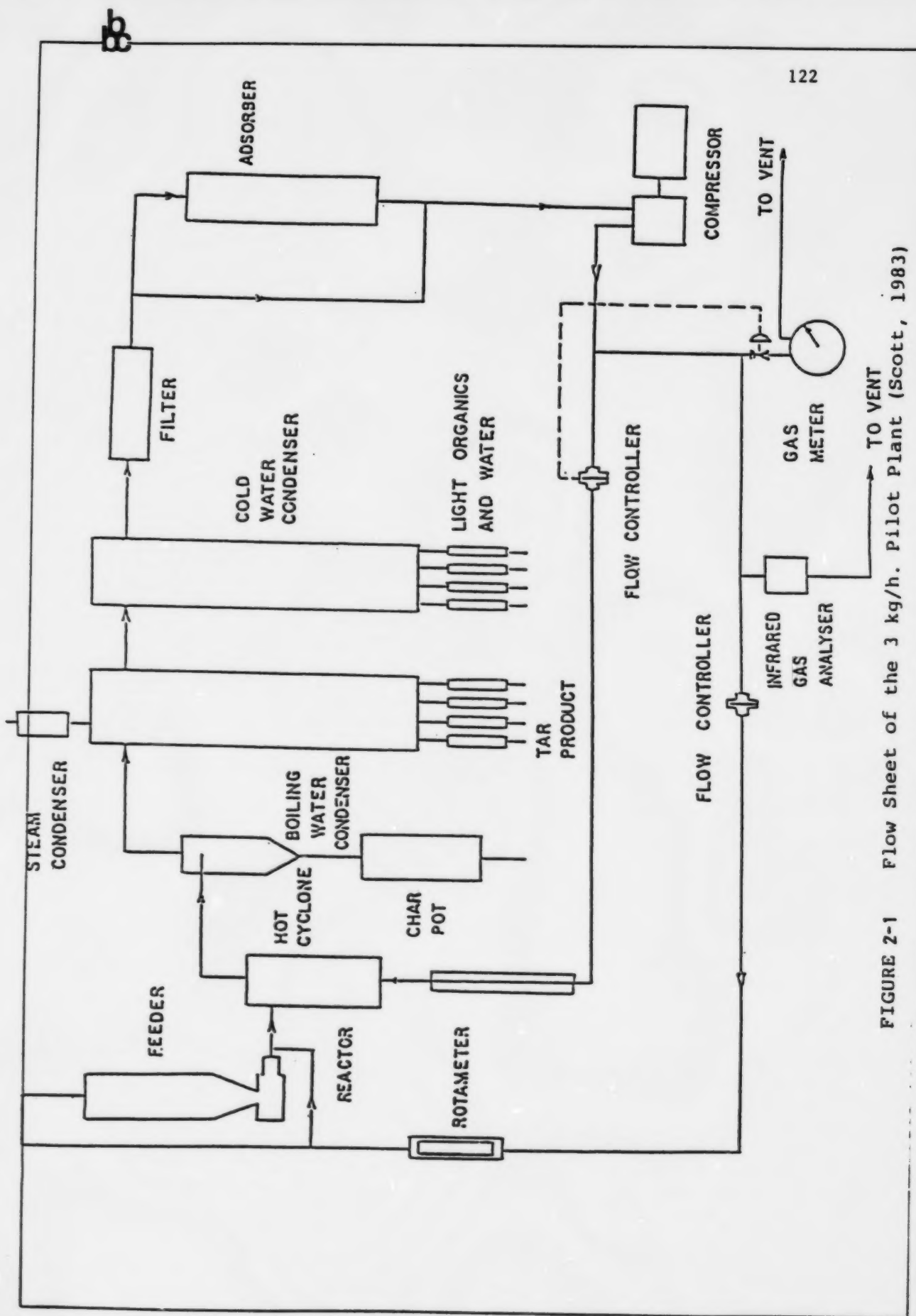


FIGURE 2-1 Flow Sheet of the 3 kg/h. Pilot Plant (Scott, 1983)

2.1 Design Criteria

The following design criteria were established for the process:

- . Normal Design Capacity - 200 bone dry Kg/hour
- . Inlet Moisture Content - 50%
- . Inlet Particle Size - Less than 25mm
- . Dryer Outlet Moisture Content - 6 to 15%
- . Grinder Outlet Particle Size - 2mm and under
- . Superficial Fluidizing Velocity - 100 to 140cm/s
- . Bed Depth - 0.35 to 0.5m
- . Residence Time in Gas Phase - 1s
- . Auxiliary Fuel - Propane
- . Two stage Liquid Condensation with interposed electrostatic precipitation

2.2 Area 100 - Material Handling

The basic premise for materials handling was that a stockpile of typical waste biomass would be made available close to the loading section of the trailer and that the material would be retrieved into the process unit on a semi-batch basis as required. This would permit operation of the trailer mounted facility close to the plant, but without hindrance to the routine operation of the manufacturing process.

In normal testing, biomass will be dumped onto a stockpile which will have a storage capacity of one to three days. The pile will

be protected from the elements by means of a tarpaulin. Material will be retrieved manually from the pile by pneumatic pick-up nozzle 101 (equipment identification numbers are identified in drawing number WA-1) and a flexible hose, at a rate of 1500 BD kg/hr. The biomass will be separated from the pneumatic air stream by combined cyclone-bag filter 102. The cleaned air will be ducted to the pneumatic blower 103 and exhausted to atmosphere. Product from the cyclone will be discharged through rotary valve 104 into a vertical lifting screw conveyor 105. In turn, the screw will transport the material to a one hour storage bin 106 fitted with a variable speed, live bottom. In order to satisfy the need to handle a wide range of materials, the bin will be straight sided, lined with low density polyethylene and fitted with a complete live bottom of transverse mounted screws.

The materials handling operator, in routine processing, will be required to load the bin for a period of ten minutes, once every hour. This is not an onerous task and it permits the storage bin to be readily fitted onto the trailer. The use of a pneumatic system will also allow some separation of heavy stones and tramp metal.

2.3 Area 200 - Material Processing and Drying

The specifications for the pyrolyser call for the feedstock to be <2mm in size and have a moisture content of about 6 to 15%...

The biomass that is typically available on location, will have a broad spectrum of particle size and moisture content.

To provide a design rationale for this situation, it was assumed that the biomass, feedstock would have a size range of 5 to 25mm with a moisture content of 50%.

For simplicity and compactness, it was concluded that a combined shredder-dryer would provide the optimum characteristics for this type of plant. Hence, this section of the process was designed around the Imp-mill flash dryer offered by Combustion Engineering.

From the intermediate storage bin 106, a controlled rate of material, 200 BD kg/hr, will be transferred into the inlet hopper of the Imp mill 201. Here the material will be evacuated through the shredder and into a short section of piping by hot air.

The material will be shredded and dried simultaneously to <2mm and 6% moisture. Other moisture levels can be obtained by modulating the flue gas inlet temperature. The grinding loop also includes classifier 202 which will return the oversize to the mill. Dry material will be segregated from the wet air by means of cyclone 204. The air will be recirculated, as needed, by blower 203, as needed, to temper the high temperature inlet gas.

Dry material from the cyclone will be discharged through rotary valve 205 into an inclined screw conveyor which transfers the feedstock to live bottom surge bin 206. The bin will have a capacity of 60 - 70 BD kg.

2.4 Area 300 - Pyrolysis and Product Separation

Area 300 is the primary process area and includes both the reactor and product separation stages.

Biomass from surge bin 206, mounted atop compression screw 301, will be partially compacted in the screw to prevent leakage of gas from the reactor. As the material exits compression screw 301, it will revert to its original texture and size by means of a cone shaped throttling device which will also serve as a method for controlling the material compression. Biomass will drop from pressurizing screw 301 into reactor feed screw 302 which, in turn, will feed directly into the fluidized bed pyrolyzer 303.

In pyrolyzer 303 the biomass will be converted into a gas, a vapourised liquid phase and a solid char by the high temperature environment in the reactor. Both the vapour and solid products will be blown out of the pyrolyzer by the hot recycled gas which is directed into the bottom of the reactor. If required, water can be injected for quenching of the gas to prevent polymerization reactions. Otherwise, the gas will directly pass into cyclone 304 for removal of char. The char will drop into cooling screw 312

and be discharged into one of two 55 gallon storage drums 401A and 401B.

Vapours from the cyclone will be cooled to 60°C or higher in the heavies condenser and pass into electrostatic precipitator 306 where the tar moisture droplets will be collected and drained to a common header which also receives liquor from the lights stream. The combined condensate will be diverted into 55 gallon drums 402A and 402B. A by-pass piping arrangement will be included so that each condensate stream can be collected separately, if desired.

From the precipitator, the gases will pass through the second heat exchanger 307 which will serve to collect water and the lower molecular weight organics, in knock-out drum 308, at 30°C. The clean gas will be evacuated through liquid ring pump 309 and recycled to the pyrolyser. Excess will be vented to flare 403.

The fixed flow of recycle gas will be preheated to 750°C in indirect heat exchanger 311 before entering the pyrolyzer. Energy for heating the gas will be provided by propane preheater 310. Flue gas from the preheater, after passing through the recycle gas heat exchanger, will be used in the drying stage.

2.5 Area 400 - Product Storage and Disposal

There are three product streams, gas, liquids and char. Gas, excess to that required for fluidizing, will be vented through flare 403, serviced by a propane pilot. The char will be deposited into 55 gallon drums 401A and 401B at a rate of 33 kg/hr or one drum every 50 minutes. Two discharge ports will be provided so that one drum can be changed while the other is on line.

A similar duplex discharge, 402A and 402B will be provided for the liquid product. Liquid production is 160 kg/hr or one drum every 80 minutes. A trolley will be included to assist in moving drums.

Drums can be shipped within the plant for fuel testing or transported elsewhere.

2.6 Auxiliary Services

A propane liquid storage facility will be provided with a capacity of 1,200 litres. Similarly a bank of nitrogen cylinders will be available for purging of containers.

Cooling water, 75 lpm, will have to be piped to the unit at each location, as will electricity. A central motor control centre will be provided on the trailer. Total power requirements are 95 kW at 575 V, 3 phase. A one-line electrical sketch is shown in drawing no. WA-2.

2.7 Instrumentation and Controls

The preliminary instrumentation drawing, WA-3, provides a composite of the instrumentation, control and data acquisition systems.

2.7.1 Control Loops

The primary control loop for the pyrolysis system centres around the need to provide a constant, preselected temperature in the fluidized bed pyrolyzer. Typically, this temperature will be 500°C, although some variation may be required to optimise the process for different types of biomass.

The temperature in the pyrolyzer is maintained by balancing the flow of energy in the recycle gas with the energy required to pyrolyze the biomass. Thus there are two ways to control the reactor temperature:

- . Adjusting biomass flow
- . Varying recycle gas flow and/or inlet temperature

To maintain consistent fluidization conditions in the pyrolyzer, it has been concluded that the recycle gas flow should be kept constant. Secondly, the gas preheater has been designed to operate close to its upper

metallurgical temperature limit. Therefore it is preferable to design the preheating system to provide a fixed outlet gas temperature. This will also simplify the control of the preheat burner.

Consequently, it is recommended that the pyrolyzer temperature be controlled by modulating the biomass flow rate. This technique will permit the system to handle a broad range of biomass materials while tolerating modest fluctuations in moisture content, around the design value of 6 - 15%.

Thus temperature control will comprise a temperature indicator controller, TIC-1, which in turn will send a signal to the motor speed control, SC-1, of the variable speed drive in the compression screw. To ensure controlled biomass flow through the compression screw, the level of the surge hopper above the screw will be maintained above a minimum specified level, by means of control loop LC-2. This loop, LC-2, will modulate the speed of the drive on the discharge screw of the primary storage bin, by means of a compensating circuit activated by 3 or 4 level switches in the surge bin.

A secondary control loop TIC-3, will be added to modulate the inlet temperature of the drier by adjusting

the flow of hot flue gas from the recycle gas preheater. This loop will be used to control the moisture content of the biomass fuel. Direct moisture control by monitoring the humidity of biomass entering the surge hopper, while possible, is not considered practical at this time. To date, moisture meters have not been found to be consistently accurate, especially when measuring different types of biomass. Instead, samples from the dryer will be analyzed by an infra-red moisture meter. The results of these tests can be made available within 30 minutes which should provide adequate response for drying.

Another control loop is also required to maintain temperatures around the recycle gas preheater. Controller TIC-4 will modulate the rate of flow of propane to the preheat burner in order to provide a constant outlet temperature for the hot recycle gas. A second controller TIC-5, will establish the inlet flue gas temperatures entering the preheater by controlling the air:fuel ratio in the preheat burner. An over-temperature switch TSH-6, will be added to shut down the preheater to prevent thermal stress on the recycle gas heat exchanger.

A flow controller FIC-6, has been included to provide a constant mass flow of gas to the pyrolyzer by venting the excess gas through CV-6. A level switch, LS-7, will prevent overfilling the primary storage bin, by shutting down the pneumatic system blower.

2.7.2 Instrumentation

The plant will include thermocouples to monitor temperatures throughout the system. This will ensure that good energy balances are obtained and will allow the monitoring of the heat exchangers' performance, particularly for tar accumulation. These thermocouples will also provide data for scale-up of ancillary equipment.

The flow of recycle gas and excess gas will be measured by orifice meter or flow averaging probes provided with pressure transducers. Continuous infra-red gas analysers will be included to monitor the CO and CO₂ concentration in the vent gas.

Both the char and liquid production rates can be measured by weighing the product drums. Biomass flow will be evaluated by mounting the primary storage bin on load-cells and following the weight loss with time.

To complete the mass balance, the char and liquor will be analysed off-site. The biomass moisture and composition will be evaluated similarly, from grab samples removed from the surge bin.

Differential pressure measurements will also be provided at key points to monitor:

- . Plugging in the case of cyclones and heat exchangers.
- . Accumulation or loss of material in the fluidized bed reactor.

2.7.3 Data Acquisition

Since no high speed or sophisticated data acquisition is required by the process, the system will be provided with an IBM-AT or compatible computer complete with analogue data acquisition boards and software.

Programs such as Lotus Measure and Lotus 123 are well suited to this type of application, where presentation of data is more important than complex manipulation of numbers.

3.0 MECHANICAL ARRANGEMENT

The entire plant will be mounted on a trailer 12m long x 2.44m wide. To provide adequate height to eliminate the need for field erection, a low-boy trailer will be used to support the equipment. Overall height of the trailer and equipment will be held to 4.11m.

The basic equipment layout is shown in drawing WA-4. The trailer will include a goose-neck so that it can be mounted behind a standard tractor. The latter can be rented with a driver for each relocation of the system.

Upon arrival at a new site, both water and electricity will have to be hooked up to a central location on the trailer.

4.0 EQUIPMENT SPECIFICATION

Following calculation of the process design parameters, detailed equipment specifications were prepared. These are described in the subsequent pages.

(See Appendix 2)

5.0 CAPITAL COST

A preliminary capital cost estimate was evaluated direct from manufacturers' quotation and from in-house resource information for similar equipment.

To this estimate was added an installation estimate for a shop erected plant.

Engineering and contingency were also included. The final estimate, \$926,500.00 is shown in Table 5-1. Taxes, if applicable, are extra.

TABLE 5-1Preliminary Capital Cost Estimate

<u>Equipment</u>	<u>Cost</u> <u>(\$)</u>
Major Process Equipment:	
Pneumatic Conveying System	30,000
Elevator Screw	9,500
Intermediate Storage Bin	20,000
Shredder Dryer	80,000
Surge Bin	15,000
Inclined Screw	5,000
Compression Screw	60,000
Feed Screw	10,000
Pyrolyser	20,000
Char Cyclone	10,000
Heavies Cooler	15,000
Precipitator	12,000
Lights Cooler	42,000
K.Q. Drum	3,000
Recycle Blower	9,000
Preheat Burner	15,000
Preheater	21,000
Ash Screw	7,000
Ash/Liquor Bins (4)	5,000
Flare	<u>15,000</u>
	403,500
Trailer	60,000
Miscellaneous Equipment	<u>3,000</u>
TOTAL EQUIPMENT COST	466,500
<u>Installation</u>	
Equipment Mounting	60,000
Instrumentation	60,000
Piping and Valves	40,000
Electrical (including wiring)	27,000
Insulation and Painting	7,000
Structural Steel	12,000
Engineering	100,000
Contingencies at 20%	<u>154,000</u>
TOTAL CAPITAL COST (taxes are extra)	926,500

6.0 ENVIRONMENTAL

There are a number of emission sources from the plant, most of which are adequately treated within the mobile system. These include:

- . Dust emissions from the vent of the pneumatic conveying system which are collected by filtration through a cloth bag filter. This type of filter is highly efficient and any discharge will be well within environmental guidelines.
- . Dust emissions from the drier exhaust. These are dedusted in a high efficiency cyclone and this should be adequate for most situations. Unfortunately, really fine material, less than 10 microns, will probably escape the cyclone. While bag filters could be added to remove these fines, the wet exhaust gas, combined with the intermittent nature of the operation, will cause serious problems for this type of dust removal equipment. Alternate methods, i.e. wet scrubbing or electrostatic precipitation, could be used but they are expensive and, in the case of wet scrubbing, there is an additional effluent stream. Because of the limited duration for operation of the plant and the reasonable efficiency of the cyclone, it was not thought justifiable to add more complexity in this instance.
- . Ash and char from the pyrolyzer are removed by a cyclone and collected in 55 gallon drums. These can be removed for safe disposal. Fine ash passing through the cyclone will almost

certainly be caught through entrapment by mist formation and be removed in the wet precipitator.

- . Most of the pyrolysis liquids will be condensed and collected in 55 gallon drums. These too can be readily disposed of in an approved facility. Any liquid mist not collected will be safely combusted in the flare.
- . Excess process gas from the system will also be flared. This is currently an acceptable technique for disposal.

There is one other stream which has not been mentioned, the cooling water from the liquid ring pump. Pyrolysis liquids will most likely be present in this but at very low concentrations. It is recommended that this, too, be collected in drums, until it can be determined if it can be safely disposed of by sewerage.

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APPENDIXIllustrative Equipment Brochures

1. Elevator Screw
2. C.E. Imp Mill
3. Compression Screw Feeder
4. Liquid Ring Pump

Available in original copy

8. Conclusions

In several ways, the present program of work has laid the foundations for the exploitation of the fast pyrolysis process as applied to biomass as a source of chemical products. The crude pyrolysis oil can be easily separated by a simple water extraction step into a fraction derived from lignin, essentially aromatic in character, and a water soluble fraction, derived from carbohydrates, which is alicyclic in nature and rich in carbonyls and hydroxy compounds. The "pyrolytic lignin" fraction is not contaminated or derivatized in any way, as are other commercially produced lignin products, but is a degraded lignin of low molecular weight, rich in phenols. It should be useful as a co-polymer in wood adhesives or in other polymeric formulations where colour is not a factor.

The water soluble carbohydrate derived fraction is rich in hydroxyacetaldehyde and in acetic and formic acids. Hydroxyacetaldehyde is difficult to recover in a reasonably pure form because of its reactivity and high solubility. However, methods such as preferential adsorption on molecular sieves can produce a solution rich in hydroxyacetaldehyde which could be used as a monomer in polymer formulations, especially for cross-linking. Acetic and formic acids can be readily recovered from the crude product in about 60% yields by simple vacuum distillation, without significant degradation of the residual crude pyrolysis liquid. It is relatively easy to produce a calcium acetate/formate or calcium magnesium acetate (for de-icing service) from this distillate.

If wood is pretreated by mild acid hydrolysis so that pentosans are removed and then pyrolyzed, a complete change in product spectrum results. Very little acetic acid or hydroxyacetaldehyde is produced, and after separation of the pyrolytic lignins, a solution rich in anhydrohexoses and hexoses is obtained. Up to an 80% conversion of cellulose to glucose can be achieved with a resulting solution concentration of 150 to 300 g/l of fermentable sugars. This approach represents a new method for the conversion of cellulose to glucose which by-passes the expensive enzymatic hydrolysis step now considered to be the best method to obtain concentrated glucose solutions. The formation of levoglucosan or of hydroxyacetaldehyde appears to occur by primary parallel decomposition paths, and it is possible to control the mechanism to produce mainly one or the other.

Primary tests have been done to evaluate the possibility of direct conversion of cellulose to hydrocarbon of C_3 or higher. Considerable success has been experienced using a fluidized bed at 500°C and atmospheric pressure in obtaining a good yield of hydrocarbons - higher than that reported by other processes such as ablative pyrolysis or ultra pyrolysis. Carbon conversion to hydrocarbons was 58.3%, and excluding methane, 33.4% of carbon fed was converted to C_2+ hydrocarbons, 93% of which was C_3 or heavier. For example, in one run 14.4% of the cellulose fed was converted to propylene or heavier olefins in this modification of the WFPP, versus a yield of 1.1% of C_3+ hydrocarbons from ultrapyrolysis. This yield of higher olefins

represents about 29% of an ideal theoretical maximum in which all C and H fed would appear as C_3+ hydrocarbon in the product. If yields approaching 50% can be obtained, the process might be economically viable at current prices. In any event, this development represents a unique direct simple one step transformation of biomass to light liquid hydrocarbons. Further results are being withheld until patents have been filed.

A mobile demonstration unit, trailer mounted, has been designed by BBC Engineering. For a feed rate of 200 kg/h of dry wood a capital cost of \$926 000 is estimated. This unit represents a scale-up factor of 50 to 100 from our present pilot plant size.

The present status of the various alternatives now available for the Waterloo Fast Pyrolysis Process are shown schematically in Figure 8.1. In fact, the WFPP now represents a group of four processes, capable of producing a variety of fuels or chemical products from a wide variety of feedstocks. Indeed, one of the features of the WFPP is its flexibility in accepting various types of biomass as feedstock. It is hoped to attract industrial collaboration in proceeding with the next stage of scale up of the Waterloo Fast Pyrolysis Process to a Process Demonstration Unit.

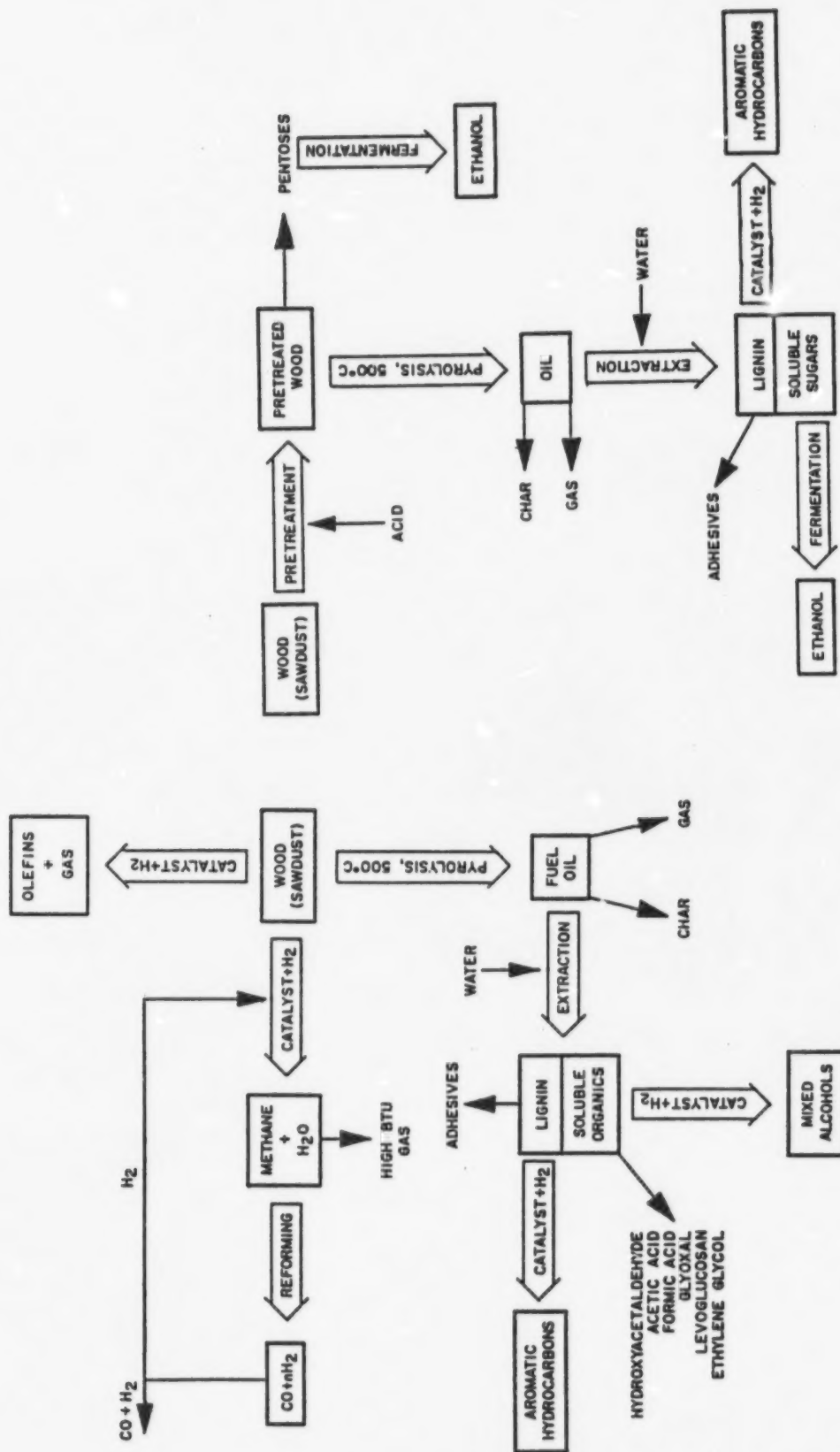


Figure 8.1 THE WATERLOO FAST PYROLYSIS PROCESSES

Fuel Oil and Chemicals
Direct Production of Hydrocarbons
Production of Sugars and Alcohol

9. RECOMMENDATIONS

If reference is made to the present processing possibilities represented in Figure 8.1 for the WFPP, the areas in which additional basic research is still needed are indicated. Which of these areas should be given priority will depend on some preliminary economic estimates of the value added potential for each. Insofar as the present state of our scientific and technical knowledge permits, and based on presently realized results, a recommended list of priority research areas for further development of WFPP processes is given below, approximately in estimated order of present value.

- a. The production of high yield sugar syrups of high fermentable sugar content from cellulose and from wood, and the testing of these syrups for use as fermentation substrates. Economic analysis of a conceptual production process.
- b. The use of pyrolytic lignin as a phenolic monomer in adhesive or other polymeric formulations.
- c. The recovery of a concentrated solution of hydroxyacetaldehyde and some market studies of possible uses.
- d. The characterization of char from wood or peat, and assessment of possible uses.
- e. Improved recovery of acetic and formic acids, and their use in the manufacture of de-icing salts.

- f. Improvement of yields of C_3+ olefins by direct conversion of biomass.
- g. Testing of an integrated hydrogasification process for wood at a bench scale level.
- h. Upgrading of pyrolytic lignin, or of wood oil to higher value fuels or chemicals.
- i. Combustion tests of wood or peat oil on a semi-industrial scale.
- j. Optimization of the product collection system for the WPPP.

The latter two recommendations could only be carried out if a Process Development Unit is available.

The first eight of these recommendations are currently under study to some degree in our laboratories. In particular, economic estimates are required, even if only very approximate, to guide future research into the most promising avenues.

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11. APPENDICES

11.1 Preliminary Results of Catalytic Studies

Hydrocarbons from Cellulose or Wood with the WFPP

In our earlier studies, it was found that by replacing the sand in the fluidized bed reactor with an appropriate catalyst, that wood could be converted in high yield to methane (about 75% carbon fed converted to CH_4). This hydrogasification was achieved at 500° to 550°C, 0.5 seconds residence time, and one atmosphere absolute pressure in a hydrogen atmosphere using a nickel on alumina catalyst. Therefore, the reactor conditions were essentially the same as those for non-catalytic operation of the WFPP.

Our speculations about the mechanism of this methanation have led us to investigate other catalytic conversions, particularly of cellulose. Some runs with poplar wood have also been tried. As a result, it appears that cellulose and some hemicellulose can be converted to $\text{C}_3\text{-C}_6$ hydrocarbons directly, with yields (based on carbon conversion) which are promising.

A number of catalysts have been screened for their action in the conversion of Avicel cellulose to hydrocarbons. At least three of these showed unique and promising results. Table 11.1 shows the data for one of these catalysts for one run. Carbon conversion to hydrocarbons was 58.3%. Excluding methane, 33.4%

Table 11.1

Run 15 M

H₂, One Atmosphere, Feed Avicel 102

Temperature 508°C

Residence Time 0.56 seconds

Feed Rate 34.7 g/h Feed/Catalyst Ratio, hr⁻¹ 1.04Yields % wt. of maf feed

Char	6.48
Tar	6.20
Water	37.31
Gas	<u>49.04</u>

Total Recovery 99.02

"Ultrapyrolysis" (850°C, 335 ms)

CO	11.55	73.40
CO ₂	5.94	5.87
CH ₄	14.29	7.00
C ₂ H ₄	1.04	8.35 + 1.63 C ₂ H ₂
C ₂ H ₆	1.78	0.78
C ₃ H ₆	2.32	1.10
C ₄ ⁺	12.12	0 ←
Total unsaturates	15.48	11.08
Total hydrocarbons C ₂ ⁺	= 17.26%	11.86
Total hydrocarbons	= 31.55%	18.86
C conversion to hydrocarbon = 58.31%		

Typical C₄⁺ products (major peaks in GC-MS analysis)

1-methyl-1,3-cyclopentadiene

1,3,5-hexatriene

1,3-cyclohexadiene

5-methyl-1,3-cyclopentadiene

3-methyl, cyclopentene

3-methyl-1,4-pentadiene

2-methyl furan

2-butanone

Cyclopentene

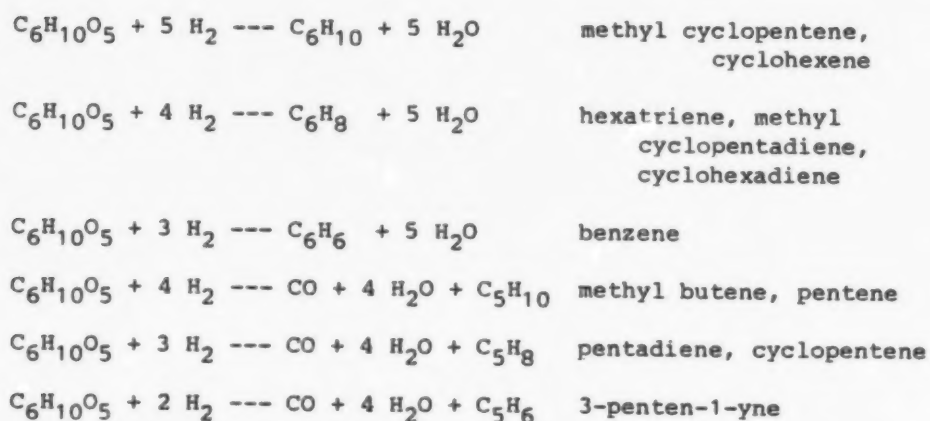
Toluene

2-propenylidene cyclobutene

3-penten-1-yne

of the carbon was converted to C_2+ hydrocarbons, primarily unsaturated. The C_2+ unsaturated hydrocarbon yield was 15.5% of the cellulose fed and 93% of that is C_3 or higher hydrocarbons.

Some typical unsaturated compounds produced were identified by GC-MS and are listed in Table 11.1. The nature of these compounds suggests the following possible stoichiometry,



All of the above reactions are thermodynamically favourable at 1 atm and 500°C.

We believe this series of reactions from a single step catalytic reaction of cellulose at one atmosphere and moderate temperatures to be unique. While the yields for C_4+ are not high, they are higher than any other pyrolysis process for the production of unsaturated hydrocarbons, and yield far larger amounts of C_5 and C_6 hydrocarbons. A comparison to the "ultra-pyrolysis" of Avicel reported by Mok et al. (Bioenergy 84, Vol. III, p.23, H. Egnéus and A. Ellegard (eds), Elsevier, 1985)

shows a total hydrocarbon production at the best conditions (850°C, 335 ms time) of 18.9%, with 8.4% being ethylene, 7.0% methane, 1.1% propylene and zero hydrocarbons C_4 or above. Unsaturated hydrocarbons were 11.1%, mostly ethylene, compared to 15.5% from the Waterloo process, mostly C_5 and C_6 unsaturated alkenes. The Waterloo process has a hydrogen atmosphere, which ultrapyrolysis did not, but also the Waterloo process uses much lower temperatures, and gives a total hydrocarbon yield of 31.6% compared to only 18.9% from ultrapyrolysis.

This chemistry to produce C_5 and C_6 unsaturates is so unusual and achieved so easily, that we believe it should be pursued. The use of pressure might significantly increase yields and it is very likely that synthesis gas could be used in place of hydrogen as a reactive atmosphere. We do not yet claim this as an economical way to make gasoline at the present level of yields, but if the biomass is very cheap (say a waste wood not required for fuel), then the economics are encouraging even at today's conditions. The C_5 and C_6 unsaturated hydrocarbons produced have very high octane numbers (ca. 150) but also can lead to gum formation in gasolines. Therefore, they would probably be used as feed stock to yield a high octane polymer gasoline. Some modest increase in yield could make this process of commercial interest in the near future.

We have results for the most effective catalysts showing the effect of variation in catalyst composition, residence time, feed to catalyst ratio, and temperature, on the yields of hydrocarbons. Three runs with wood are planned to conclude this phase of the investigation.

Because of the novelty of these results, this report should be held as **CONFIDENTIAL** pending a decision to take out a patent application.